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THE

PHYSICAL REVIEW

ARE QUANTA UNIDIRECTIONAL?

G. BREIT

ABSTRACT

Theory of the Brownian motion of a Planck radiator in black body radiation.—*In the case of a classical resonator* it is shown that the motion takes place even though the emission and absorption is not unidirectional provided the radiation is not strictly monochromatic. This theory is then extended to *the case of a quantized atom.* Interference between the waves emitted by the atom and the surrounding radiation provides for the recoil actions without the assumption of unidirectional quanta. Statistically these have the same effect as Einstein's unidirectional quanta. This theory removes the contradiction postulated by Einstein between the Rubinowicz-Sommerfeld considerations and the requirements of classical Brownian motion. It leaves the wave-theory of light intact and is in agreement with Bohr's principle of correspondence.

INTRODUCTION

EXPERIMENTS on the development of photographic plates, on the photoelectric effect as well as the theoretical considerations of Einstein and Schroedinger[1] support the belief that quanta are darts of light, i.e. that the electromagnetic momentum of a quantum is in the same direction for all of its energy. Neither of these is a case of conclusive evidence. The photographic and photoelectric experiments indicate only the places where energy is absorbed and it appears that the only considerations dealing with the momentum of the quantum are the theoretical ones just cited. The fundamental point is contained in the paper of Einstein. This is verbally quoted as a proof of the unidirectional nature of quanta. In the paper there appears to be no statement to this effect though it shows that if it be granted that quanta are darts of energy

[1] A. Einstein, Phys. Zeits. **18**, 121, 1917
E. Schroedinger, Phys. Zeits. **23**, 301, 1922
L. Silberstein and A. H. Trivelli, Phil. Mag. **44**, 956, 1922
L. Silberstein, Phil. Mag. July 1922, p. 257
Svedberg and Andersson, Phot. Journ. August 1921, p. 325
Svedberg, Phot. Journ. 1922, pp. 183-186

the conditions of correct Brownian movement are satisfied. The legitimacy of the converse proposition is not evident—nor does the writer think it is true—though at first sight it is difficult to see in what way the conditions will be satisfied unless the hypothesis of light darts is made.

In this note an alternative to Einstein's treatment is presented which makes it unnecessary to assume the unidirectional nature of quanta.

Similar Problem in Classical Theory

This problem was first discussed by Einstein and Hopf[2] who showed that the requirement of correct Brownian movement of a classical resonator necessarily leads to the Rayleigh-Jeans formula. The discussion given below is not essentially different from that of Einstein and Hopf. It calls attention however to some features of the problem which are of importance in connection with the quantum case.

Let us first see how classical electrodynamics explains the Brownian movement of a Planck resonator in a black body radiation.

For simplicity let the resonator have an axis the orientation of which is fixed, and let its motion of translation be confined to that in a straight line which we choose as the axis of X (OX) and which we take as the resonator's axis. We shall suppose the resonator attached to a particle of large mass M so that the translational velocity of the resonator is always small compared with that of light. The calculation will be similar to that used by Einstein.

We consider the beginning and the end of a fixed time interval τ and we change the beginning and the end at random keeping τ constant. We take the mean square of the momentum for the beginning and for the end and we express the fact that the mean square is the same for both. If the velocity at the beginning of the interval is v, if the systematic resisting force is Rv and if the summation of the accidental random impulses is Δ

$$\overline{(Mv-Rv\tau+\Delta)^2}=\overline{(Mv)^2}$$

and

$$\overline{\Delta^2}/\tau=2RkT \tag{1}$$

The origin of the resisting force Rv lies in the fact that there is a relative motion between the resonator and the radiation (the velocity v). The force Rv is of the same nature as radiation pressure and will have essentially the same expression in Einstein's theory and this.

The origin of Δ is not quite so simple. It lies in the spectral width of the band absorbed by the resonator because the absorption of one frequency

[2] Einstein and Hopf, Ann. der Phys. **33**, 1105, 1910. I am indebted to Professor Sommerfeld for this reference.

by a resonator put in the well known cube of Jeans' does not give any recoil action on account of the stationary character of the waves.

The resonator responds however not to a single frequency but to a band. Consider stationary waves of frequencies ν_1, ν_2. The electromagnetic momentum of the sum depends on $[E_1H_1]+[E_2H_2]+[E_1H_2]+[E_2H_1]$ where E, H are the electric and magnetic intensities corresponding to ν_1 and ν_2. The first two terms of the above expression correspond to the waves acting separately and give no flux during a time large in comparison with the period. The last two terms represent the interference effect of the waves. They give terms of the form $\sin(\omega_2-\omega_1)t$ where $\omega=2\pi\nu$ and thus correspond to long period oscillations in the electromagnetic momentum.

Calculation of Δ. For this we avail ourselves of a result of Planck.[3] Planck is concerned with an oscillator having a charge e, a mass m, exposed to radiation of energy density $6T_\nu d\nu$ in the frequency range $(\nu, \nu+d\nu)$. The energy of the oscillator itself is denoted by ϵ and the amount of energy absorbed by the oscillator from the field is η_e. Planck considers η_e^2 for a time τ and takes its average value. The result is

$$\overline{\eta_e^2}=\frac{e^2}{2m}T_\nu\epsilon\tau \tag{2}$$

Now the energy absorbed by an oscillator is the work done on it by the external field. In the time between two instants t_1, t_2 this work is

$$\eta_e=\int_{t_1}^{t_2} eE_x\dot{\xi}dt \tag{3}$$

where E_x is the component of the external electric field taken along the axis of the resonator and $\dot{\xi}$ is the velocity of the oscillator's electrified particle having the charge e.

The force on the oscillator due to the action of the magnetic field on its moving electrified particle is perpendicular to the resonator's axis and gives rise to the radiation pressure. The value of this force resolved along the line of motion of the resonator is $(eH_y/c)\dot{\xi}$ [OY being an axis perpendicular to OX and OZ] and using (2) and (3)

$$\overline{\Delta^2}=\frac{e^2}{2mc^2}T_\nu\epsilon\tau \tag{4}$$

since statistically the behaviour of E and H is the same (for justification see Note 1).

Calculation of R. For this we use formula (260) of Planck[3]

$$\overline{\eta_e}=\tfrac{1}{4}(e^2/m)T_\nu\tau \tag{5}$$

[3] M. Planck, Wärmestrahlung, 4th edition p. 153, formula (261)

This gives the average absorbed energy in the time τ. It may be shown that the radiation pressure is such as corresponds to the absorption of an electromagnetic momentum which is v'/c^2 times the absorbed energy where v' (see Note 2) is $v[3-(\nu/\rho)(\partial\rho/\partial\nu)]$. In the case of the Rayleigh-Jeans radiation formula $v'=v$ and by (5)

$$Rv=(e^2T_\nu/4mc^2)v \tag{6}$$

Using (4) and (6) it is seen that (1) is satisfied if

$$\epsilon=kT \tag{7}$$

which is true in the classical theory.

If the axis of the resonator forms an angle φ with the line of motion the terms $\overline{\Delta^2}/\tau$, R are found to be $\sin^2\varphi$ times the values found above. Equation (1) is therefore again satisfied in virtue of (7).

Resumé of treatment of classical case. The above derivation shows how a classical resonator reacting with the radiation by the ordinary laws of electromagnetism is maintained in a state of Brownian movement with the correct mean kinetic energy per degree of freedom ($kT/2$). The derivation is based on the similarity between the expressions for the energy absorbed and the radiation pressure. It also implies a statistical equivalence of E_z and H_y in the calculation of Δ.

The above picture does not involve the hypothesis of unidirectional emission though it is true that this hypothesis also satisfies (1). It is clear that unless some additional fact is given the mere validity of (1) will not enable one to decide between these two possibilities and we are thus inclined to doubt the possibility of such a decision in quantum theory.

Discussion of Quantum Case

Very little is known about the mechanism of absorption and emission of radiation. The discussion of the physical reality is of necessity only tentative.

It will be satisfying to make the basic phenomenon of the quantum and the classical treatment the same. Interference between the field of the resonator and the surrounding field may be thought of as fundamental in the classical theory and will be presented below as the basis of a quantum theory of Brownian movement. By so doing the apparent contradiction between the view of Rubinowicz and Sommerfeld, that the wave emitted by a Bohr atom may be spherical, and Einstein's postulate of correct Brownian movement, is removed because the spherical wave hypothesis may be conceived as satisfying Einstein's postulate in a manner analogous to that of the classical resonator.

For simplicity let us deal with an atom emitting linearly polarized light, (e.g. a quantized Planck resonator). It is feasible to suppose that the recoil action on the atom due to its emission or absorption is the same as if the same energy changes took place from a classical resonator.

We can now calculate the terms Δ and R. For the latter the calculation of Einstein can be interpreted to mean that $v' = v[3-(\nu/\rho)(\partial\rho/\partial\nu)]$ (see Note 2). Applying this to Einstein's model and preserving the relation $c^2\overline{\Delta^2} = \overline{\tau_\epsilon^2}$ (see (2), (4)) it is found that both $\overline{\Delta^2}/\tau$ and R can be obtained from his values by multiplying them by the factor 3. The relation (1) is therefore still satisfied.

The fundamental postulates of this theory are then:

(1) *The systematic resisting force Rv has the same ratio to the absorbed energy as if the quantized atom were a classical resonator moving in the actual radiation field*, here determined by Planck's formula.

(2) *The relation $c^2\overline{\Delta^2} = \eta_\epsilon^2$ is true not only in the classical but also in the quantum theory.*

In the above an atom emitting linearly polarized light, say a quantized Planck resonator was discussed. By interchanging electric and magnetic singularities the result is extended to circularly polarized light.

The writer has spoken about this subject to several people whose ideas influenced his own. He first erroneously believed that one could think consistently of a quantized atom not exchanging momentum with the radiation. In a conversation Prof. Einstein was kind enough to point out that a classical resonator experiences radiation pressure and that it would be therefore inconsistent not to introduce an equivalent of this in the quantum theory. Thus it appears that the classical analogy has been kept in mind by Einstein but that he preferred to build the theory along revolutionary lines rather than to modify the classical theory to the least extent. The subject was also discussed with Prof. Ehrenfest of Leyden, Prof. Ames of Johns Hopkins, Prof. Epstein of Pasadena, Dr. Kemble and Dr. Van Vleck of Harvard.

Note 1. Statistical Equivalence of E_z and H_y in the Calculation of $\overline{\Delta^2}/\tau$

Since E_z affects $\dot{\xi}$ and H_y does not, a justification is needed for the interchange of these in $\int E_z\dot{\xi}dt$ in the derivation of $\overline{\Delta^2}/\tau$.

The classical theory of black body radiation may be developed by considering the resonator as damped by its radiation resistance. To

within a good approximation this damping may be taken into account by a frictional term in its equation of motion[4] which we write

$$\ddot{\xi}+\kappa\dot{\xi}+\omega_0^2\xi=(e/m)E_z$$

$\kappa\dot{\xi}$ is here the frictional term. Let

$$\frac{e}{m}E_z=\int_0^\infty A(\omega)\cos(\omega t-\varphi_\omega)d\omega.$$

Then

$$\dot{\xi}=\int_0^\infty \frac{A(\omega)\cos\{(\omega t-\varphi_\omega-\tan^{-1}[(\omega^2-\omega_0^2)/\kappa\omega)]\}}{\sqrt{\kappa^2+[(\omega^2-\omega_0^2)/\omega]^2}}d\omega$$

We are interested in the average square of the integral from t_1 to t_2 of $(e/m)E_z\dot{\xi}dt$. Replacing integrations as to ω by summations, multiplying the expressions and integrating with respect to the time, we obtain terms of the types $A(\omega_1)^2$ and $A(\omega_1)A(\omega_2)$. The latter type is subject to double summation as to ω_1 and ω_2 and it contains a set of terms having in the denominator $\omega_1-\omega_2$. When the result is squared these terms give the main contribution to the average if $\tau=t_2-t_1$ is a short time in comparison with that necessary for the development of E_z into the Fourier series. These terms give

$$\sum{}'\frac{A(\omega_1)^2\,A(\omega_2)^2}{4}\;\frac{\cos^2\psi\sin^2(\omega_1-\omega_2)\tau+4\sin^2\psi\sin^4\frac{1}{2}(\omega_1-\omega_2)\tau}{(\omega_1-\omega_2)^2\{\kappa^2+[(\omega_1^2-\omega_0^2/\omega_1)]^2\}}$$

where $\psi=-\varphi(\omega_1)-\tan^{-1}[(\omega_1^2-\omega_0^2)/\omega_1]+\varphi(\omega_2)$ and the summation is taken over all values of ω_1, ω_2 excluding $\omega_1=\omega_2$. It is clear now that if $A(\omega_2)$ be replaced by $B(\omega_2)$ and if $\overline{A(\omega_2)^2}=\overline{B(\omega_2)^2}$ the result of the summation is unchanged on account of the random nature of $\varphi(\omega_2)\;\varphi(\omega_1)$. This and a random change in the φ's is all that is required in order to replace E_z by H_y. Thus the validity of the interchange is justified. Taking the average and replacing the sum by an integral the average value becomes $(\pi^2/8)(A^2/\delta\omega)^2(\tau/\kappa)$ where $\delta\omega$ is the difference between two successive ω's in the summation. This is readily seen to be identical with the expression of Planck.

The occurrence of the terms $\omega_1-\omega_2$ shows the importance of the interference between adjacent frequencies for $(\overline{\Delta^2}/\tau)$.

Note 2. The Calculation of the Resisting Force on a Classical Resonator Moving in Black Body Radiation

Let E_z', H_y' be the components of the electric intensity along the resonator's axis and of the magnetic intensity perpendicular to the

[4] Kretschmann, Ann. der Phys. 65, p. 310, 1921

resonator's axis and to the axis of motion—both measured in a frame of reference moving with the resonator. The time integral of the radiation pressure is the time integral from t_1 to t_2 of $(e/c)H_y'\dot{\xi}$, where ξ is the velocity of the oscillatory particle. The absorbed energy is the corresponding integral of $e^2E_z'\dot{\xi}$. If the average over a long interval of time is desired the various frequency terms can be considered independently. The ratio of two terms of corresponding frequencies in both expressions is $(\int_{t_1}^{t_2}(1/c)\,H_y'(\omega)\cdot E_z'(\omega)dt)/(\int_{t_1}^{t_2}E_z'(\omega)dt)$ where the sign (ω) after a symbol indicates that only the term in the particular frequency discussed is taken and where it is supposed that $H_y'(\omega)$, $E_z'(\omega)$ are in phase. [The field is analyzed into a number of plane waves of different frequencies.] This ratio is the ratio of three times the density of electromagnetic momentum, resolved in the negative direction of OX, to that of the electromagnetic energy. Since resonance is sharp only a narrow band of frequencies need be considered. For this the ratio is the same throughout.

In calculating the ratio we may consider a number of independent plane waves within the band sweeping by the resonator. No interference action between these waves must be considered because their frequencies are affected by Doppler's principle to a different extent on account of the difference in direction. Thus we may use Eq. (19) of Einstein[1] which gives for the energy in the frequency range $d\nu$ per unit solid angle in a direction making an angle φ with the line of motion

$$\frac{1}{4\pi}\left(\rho+\frac{v\nu}{c}\cdot\cos\varphi\cdot\frac{\partial\rho}{\partial\nu}\right)\left(1-\frac{3v}{c}\cos\varphi\right)d\nu$$

where $\rho d\nu$ is the energy density with respect to the container. Multiplying this by $-\cos\varphi/c$, integrating, and dividing by $\frac{1}{3}\rho d\nu'$ the ratio of radiation pressure to energy absorbed per unit time is

$$(v/c^2)\,[3-(\nu/\rho)(\partial\rho/\rho\nu)]=v'/c^2$$

where $v'=v[3-(\nu/\rho)(\partial\rho/\partial\nu)]$. In the classical theory ρ is of the form $a\nu^2$ and $v'=v$.

NATIONAL RESEARCH FELLOWSHIP,
CRUFT LABORATORY, HARVARD UNIVERSITY,
March 1, 1923.

THE EFFECT OF A MAGNETIC FIELD ON THE ABSORPTION OF X-RAYS

By Joseph A. Becker[1]

Abstract

Effect of a magnetic field on the absorption of x-rays.—A continuation of previous work (Phys. Rev. **20**, p. 134, 1922) with improved specimen holders and technique. *Iron, aluminum, and carbon* showed no changes in the absorption coefficient as great as one part in 10,000 (due to a magnetic field of 17,000 gauss) when the tube was operated at 90 kv peak. *Carbon, wood, and lithium* also showed effects smaller than the limit of accuracy of the apparatus—2 parts in 10,000 for 61 kv, 4 parts in 10,000 for 46 kv, and 10 parts in 10,000 for 30 kv. If the effect exists, then, it is very small.

THIS article is a continuation of a previous article of the same title in the Physical Review for August, 1922, vol. 20, p. 134. Unless otherwise stated the procedure was the same as described previously.

The specific objects of the present investigation were (1) to design and test a new specimen holder to be used when the magnetic field H was perpendicular to the x-ray beam X; (2) to determine how closely the method of determining the relative change in the absorption coefficient due to a magnetic field could be relied upon; and (3) to extend the work to longer waves for a few low-atomic weight elements.

The new specimen holder. In the previous article doubt was expressed as to the efficacy of holder h in Fig. 1 of the previous article, in preventing slight displacements of the specimen. The new holder was built along the lines used in the construction of holder h_2, shown in the same figure. This new holder, which was used in all cases when H was perpendicular to X, rigidly held the specimen immediately in front of a lead slit or opening and prevented any mechanical effect which might be caused by the forces on the pole-pieces or by the direct action of H on the specimen.

Duplicability of results. To determine whether or not the small effects obtained were due to chance and how closely the results could be duplicated, a specimen of iron, one of aluminum, and one of carbon were tested. The following week another series of tests was performed with the same samples. The same procedure was again repeated the third week. In all these tests the peak voltage across the tube was 90 kv and the magnetic field of 17000 gauss was perpendicular to the x-rays.

[1] National Research Fellow in Physics

Fig. 1 is a typical graph of the observations. The rate of drift of the electroscope leaf in divisions per minute δ is plotted against the time in minutes. It will be noticed that the magnetic field was applied for one-half minute during each minute. The double arrow on the right shows $\Delta\delta$, i.e. the change in δ, that was produced by changing the area of one beam by four parts in ten thousand. This $\Delta\delta$ could be determined with a precision of about 10 per cent.

TABLE I

Results for a field of 17,000 gauss, perpendicular to the x-rays

	Trial no.	$\Delta\delta$ due to H	I/I_0	$\Delta I/I$ ($\times 10^{-4}$)	Max. oscill. ($\times 10^{-4}$)	$\Delta\mu/\mu$ ($\times 10^{-4}$)
Iron	1	+ 2	.45	.3	4	− .4±1
	2	+1.4	"	.4	5	− .5±1
	3	−1.5	"	−.5	4	+ .6±1
Aluminum	1	3	.55	.5	4	−.85±1
	2	1.4	"	.3	4	− .5±1
	3	0	"	0	4	− 0±1
Carbon	1	4.2	.60	.6	4	−1.2±1
	2	−1.2	"	−.2	3	+ .4±1
	3	−0.1	"	−.0	4	0±1

Table I sums up the results of this series of tests. $\Delta I/I$ gives the proportionate change in the intensity of the beam which has passed through the magnetized specimen. This is obtained by dividing $\Delta\delta$ due to H by the $\Delta\delta$ for a change in area of 1 part in 1000. The maximum oscillation is obtained by taking the difference in δ for the highest and lowest points for H on, and H off, respectively, and dividing the larger of these two oscillations by $\Delta\delta$ for $A/1000$. An effect equal to about one-fourth of this maximum oscillation could have been detected. $\Delta\mu/\mu$, the proportionate change in the absorption coefficient, is obtained from I/I_0 and $\Delta I/I$ by means of a formula developed in the previous article. The figures in the last three columns are reported as so many parts in 10,000.

It will be noticed that $\Delta I/I$ is never more than 15 per cent of the maximum oscillation. It can conservatively be concluded that *a magnetic field of 17,000 gauss perpendicular to an x-ray beam produced by 90 kv peak changes the absorption coefficients of iron, aluminum, and carbon, by less than 1 part in 10,000.*

LONGER WAVE-LENGTH TESTS

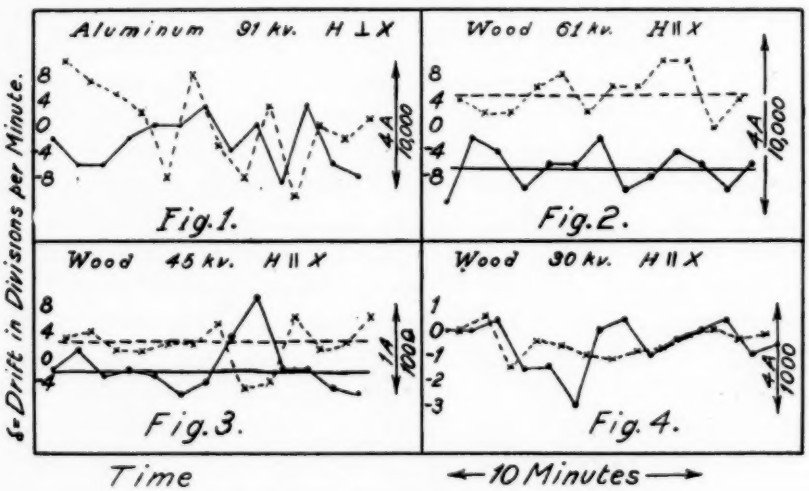
Carbon, wood, and lithium were examined with x-ray beams produced by 61, 46, and 30 kv peak with the results given in Table II. Figs. 2, 3,

and 4 show representative graphs for wood at the three voltages. Thirty kv was as low a voltage as could advantageously be used with the present apparatus.

TABLE II

Material	Peak kv	H in gauss	$\Delta\delta$ due to H	I/I_1	$\Delta I/I$ ($\times 10^{-4}$)	Max. oscill. ($\times 10^{-4}$)	$\Delta\mu/\mu$ ($\times 10^{-4}$)
Carbon	61	17000 perpend.	4.1 .6	.6	.8	5	-1.6 ± 3
Carbon	30	" "	.21	.3	5	30	$-\ 4\pm6$
Wood	61	" "	$-\ 3$ $+1.2$	.65	$-\ .3$	5	$+\ .7\pm3$
"	46	" "	$+1.8$	.6	$+1.2$	8	-2.4 ± 4
"	30	" "	.2	.5	$+\ 2$	33	$-\ 3\pm8$
"	61	11000 parallel	12	.73	$+2$ *	2	-6.4 ± 2
"	45	" "	4	.65	2.8*	11	-6.5 ± 4
"	30	" "	.05	.43	$-\ .7$	26	$+\ .8\pm7$
Lithium	91	13000 parallel	-1.0	.66	$-\ .8$	15	$+1.9\pm3$
"	61	" "	$+1.3$	.60	$+1.2$	12	-2.4 ± 3
"	45	" "	$+\ .8$	.54	$+1.9$	8.4	-3.1 ± 4

In general the effects are smaller than could be detected with certainty. In all but the two cases marked with a star in Table II, $\Delta I/I$ is less than one-fourth of the maximum oscillation. The two exceptions are plotted in Figs. 2 and 3. During the course of the present trials it was attempted



Figs. 1 to 4. •=H off; x=H on

to keep conditions as steady as was possible with the facilities described. The smallest effect which could have been detected with certainty and measured with a precision of approximately 25 per cent was 2 parts in

10,000 at 61 kv, 4 parts in 10,000 at 45 kv, and 10 parts in 10,000 at 30 kv. To measure smaller effects than these would require a complete remodelling of the apparatus, paying particular attention to (1) steady voltage across and steady current through the tube, (2) constancy of the source of potential for the plates of the electroscope, (3) symmetry of the paths traversed by the two beams, (4) stray effects of the x-rays and magnetic field, (5) mechanical jars, (6) uneven temperature effects, and (7) the specimen holders.

Summary

The results of the two papers may be summed up in the statement that magnetic fields up to 18,000 gauss do not change the absorption coefficient for x-rays generated in a tungsten target Coolidge tube by 90, 60, 45, and 30 kv by more than about 1 part in 10,000 for the higher voltages to 1 part in 1000 for the lower voltages, in some ferromagnetic, diamagnetic, low atomic weight and high atomic weight elements.

Rockefeller Hall,
Cornell University,[2]
March 21, 1923.

[2] Present address: Norman Bridge Laboratory, California Institute of Technology

THE OPACITY OF AN IONIZED GAS

By John Q. Stewart

Abstract

Theory of the absorption of radiant energy by free electrons in an ionized gas.—The classical theory of the optical properties of metals, supposed to contain free electrons, is applied to an ionized gas. As a result of collisions with molecules, vibrational energy supplied to the electrons by the electromagnetic field is transformed into energy of thermal agitation. The coefficient of absorption comes out proportional to $\lambda^2 p^2$, where λ and p are the wavelength and pressure. There is also a scattering effect proportional to p and independent of λ, but this is relatively unimportant except at pressures of 10^{-4}atm. or less. The equations developed are tentatively applied to a discussion of (1) *opacity of the vapors of exploded wires.* However Anderson reports an opacity 200 times greater than that roughly computed from theory, and varying inversely as λ or λ^2. Evidently the subject requires further study. (2) *Opacity of the solar atmosphere.* Employing Saha's theory to calculate the ionization, coefficients are computed which indicate that electronic absorption may be an important cause of the opacity of the solar photosphere. It is concluded that light from regions where the pressure is greater than .01 atm. is cut off completely, so that all we see comes from a spherical shell of rarefied gas. (3) *Opacity of giant stars.* Computations made, assuming the relation between temperature and pressure given by Eddington's theory of stellar constitution, are found in rough agreement with Eddington's values of opacity.

YEARS ago J. J. Thomson showed that, owing to scattering of radiation, an atmosphere containing free electrons should possess marked general opacity; and he suggested that this cause of opacity might be effective in the solar atmosphere.[1] Now that Saha's theory is available for calculation of the ionization, this suggestion can be quantitatively applied.

By the process of scattering, radiation is diffused in direction but not lessened in amount nor much changed in frequency. The term absorption should be reserved for those processes which result in the disappearance of radiant energy. The present paper points out that in an ionized gas collisions between free electrons and molecules theoretically result in such an absorption. These collisions transform into thermal energy of translation the vibrational energy supplied to the electron by the electromagnetic radiation field. Formulas describing this process have been worked out by Drude, Lorentz, and others in connection with the

[1] J. J. Thomson, Phil. Mag. **4**, 253, 1902

free electron theory of the optical properties of metals.[2] In the present paper these formulas are applied to conditions in an ionized gas.[3]

THEORY

The standpoint is that of classical electromagnetic theory. How far this theory represents the facts is doubtful. For this and other reasons the results of this paper are to be regarded as only tentative.

When plane waves of polarized light are advancing through an ionized gas which is not too dense, the following well-known equation applies statistically to the motion of each free electron in a layer parallel to the wave-front and thin with reference to the wave-length,

$$m\frac{du}{dt} - \frac{ma}{c}\frac{d^2u}{dt^2} + 2mru = eE. \qquad (1)$$

The mass of an electron is m, or 8.93×10^{-28}; its charge is e, or 4.774×10^{-10}; its radius is a, $=2e^2/3mc^2$, or 1.88×10^{-13}; c is the velocity of light, or 3.00×10^{10}. (In this paper c.g.s. and electrostatic units are employed throughout, except that pressures are expressed in atmospheres.) The magnitude of the alternating electric vector of the radiation field is E; t represents time; and u is that part of the component of the electron's velocity in the direction of E which is due to the action of the radiation field. The number of collisions with atoms or ions per unit time per electron, due to the thermal agitation, is r.

The electric field of the radiation exerts a force eE on each electron; the direction of this force lies in the plane of the wave-front. There is an additional force due to the polarization of the medium; but this is negligibly small unless the density of the ionized gas is very great or the frequency of the radiation low compared with the frequency of light. The magnetic field exerts a very small force (the radiation pressure) in the direction of propagation of the radiation; and this force also is negligible in the present discussion.

Eq. (1) states that the impressed force eE is balanced by three reactions. The existence of the first is obvious. The second is the well-known reaction on an electron of its own radiation, and may also be written $-(2e^2/3c^3)\ (d^2u/dt^2)$. The third is statistical; its existence is indicated by the following argument.

If a steady electrostatic field E' acts on an ionized gas, each free electron is subject to an acceleration eE'/m in the direction of the field. The effect of collisions between electrons will be neglected. Since the

[2] For example, O. W. Richardson, Electron Theory (1916), pp. 410, 432

[3] A preliminary account of the work has appeared: J. Q. Stewart, Nature **111**, 186, 1923.

mass of an electron is relatively small, the magnitude of its velocity in a given direction after a collision with an atom may be assumed uninfluenced by its velocity before the collision. Between successive collisions, then, each electron moves on the average in the direction of the field the distance $eE'/2mr^2$; so that the average velocity of drift due to the electrostatic field is $u=eE'/2mr$. Thus the average momentum of each electron in the direction of the field is $mu=eE'/2r$. Statistically the effect of collisions, therefore, can be interpreted as a frictional force on each electron of amount $2mru$. Since the velocity of drift is small compared with the average velocity of thermal agitation of the electrons, r is independent of u.

When E' is equal to unity, the magnitude of the electric current in a column of unit cross-section, or the electrical conductivity, obviously is, if there are n free electrons per unit volume,

$$\sigma=ne^2/2mr. \tag{2}$$

The current carried by the comparatively massive ions is negligible.

Returning to (1), write $E=E_0\cos 2\pi\nu t$, where ν is the frequency of the radiation of wave-length λ. The average rate s at which energy is diverted by each electron from the primary radiation is $(1/t)\int_0^t eEudt$. The intensity I of the radiation is given by $cE_0^2/8\pi$. The quantity a/λ is so small that its square may be neglected in comparison with unity. If r/ν likewise is small, as is true in the cases to be considered, it follows from (1) that

$$s=(3/\pi)\ (2\pi^2a/\lambda+r/\nu)a\lambda I. \tag{3}$$

If $r=0$, as for an isolated electron, all of the diverted energy is reradiated—"scattered"—with frequency unchanged (to the first order of small quantities); and no energy of the radiation is transformed to heat. The energy scattered per unit time per electron is[4]

$$s_1=6\pi a^2I=(8\pi e^4/3m^2c^4)I=(6.7\times10^{-25})I, \tag{4}$$

when s_1 and I are expressed in c.g.s. units.

When r is not zero, the average rate at which heat is developed per unit volume is, from (3), $3nrac^2E_0^2/8\pi^2\nu^2$. This may be written $\frac{1}{2}\sigma_\nu E_0$, where σ_ν, thus defined, is the electrical conductivity of the ionized gas for alternating current of frequency ν. Accordingly, provided r/ν is small, and making use of (2),

$$\sigma_\nu=n^2e^4/4\pi^2m^2\nu^2\sigma, \tag{5}$$

nearly.

The physical significance of (3) is better brought out by writing it in the form,

$$s/r=(4\pi^2a\nu/\lambda r)\phi+2\phi. \tag{6}$$

[4] L. Page, Astrophys. J. **52**, 67, 1920

Obviously s/r is the energy diverted per electron per collision interval. The quantity ϕ is the maximum kinetic energy of vibration of an electron due to the radiation; its value is easily shown from (1), when r/ν is small, to be $(3a\lambda^2/2\pi c)I$, since the maximum velocity attained in the simple harmonic vibration is, nearly, $eE_0/2\pi m\nu$. According to (4) the amount of energy scattered per electron per vibration is

$$(6\pi a^2/\nu)I=(4\pi^2 a/\lambda)\phi.$$

Thus the first term on the right hand side of (6) represents the energy scattered by an electron during the time between two successive collisions. (Collisions are assumed instantaneous). Evidently, then, (6) implies that at the average collision, twice the maximum vibrational kinetic energy of an electron in the radiation field is transformed into disorganized heat-molecular energy. The appropriate assumptions about the nature of collisions should immediately give this result, without going through (1) with its statistical term $2mru$. Another supporting line of argument has been given by Lorentz, in connection with the effect of molecular collisions on bound electrons. He has shown[5] theoretically that if an electron is given r random blows per unit time the resultant term due to such "impact-damping" in the equation corresponding to (1) is $2mru$.

Eq. (3) can also be written

$$s=(8\pi e^4/3m^2c^4)I+(2e^2r\lambda^2/\pi mc^3)I, \tag{7}$$

or, in c.g.s. units,

$$s=(6.7\times10^{-25})I+(16.0\times10^{-24})r\lambda^2 I.$$

The first term, or s_1, expresses the amount of energy scattered, the second term s_2, the amount of energy absorbed, per unit time per electron. Write

$$K=K_1+K_2=ns_1/I+ns_2/I.$$

Then K_1 is that part of the opacity coefficient K which is due to scattering, and K_2 is the part due to absorption.

It may be shown that the intensity I of radiation in the direct transmitted beam emergent from a layer of ionized gas of thickness z, when the intensity in the incident beam is I_0, is given by

$$I=I_0\epsilon^{-Kz}, \tag{8}$$

where ϵ is the base of natural logarithms. By (3) the ratio between the energy scattered in unit time per electron and the energy absorbed is $2\pi^2 a\nu/\lambda r$, a ratio which, owing to the decrease in r, increases with decreasing pressure of the gas. If scattering is appreciable the total amount

[5] H. A. Lorentz, Proc. Amsterdam Acad. **8**, 591, 1905, and other papers in the same Proceedings.

of light transmitted is greater than that which gets through in the direct beam.

Before (7) can be applied it is necessary to obtain an expression for r in terms of known quantities. As the kinetic theory of an ionized gas is an unexplored field, the following argument may be greatly in error. Assuming equipartition of energy between molecules and free electrons, the root-mean-square velocity of a free electron in a gas is given by $\sqrt{(3RT/m)}$, where R is the gas constant per molecule, or 1.37×10^{-16}, and T is the absolute temperature. This reduces to $(6.8\times10^{5})\sqrt{T}$. The length of the electronic free path is $1/\pi NA^2$, where N is the number of atoms in unit volume, whether ionized or not, and A is the radius of an atom (assumed independent of ionization, an assumption doubtless incorrect). In most cases of astrophysical interest the ionized gas is presumably monatomic. Thus (nearly enough),

$$r=\pi NA^2\sqrt{(3RT/m)}. \tag{9}$$

Write $n=Ni$, so that i is a numerical factor expressing the average amount of ionization. Also write $N=273\ N_0p/T(1+i)$, where p is the total gas pressure in atmospheres, including the pressure $ip/(1+i)$ of the free electrons, and N_0 is the number (2.705×10^{19}) of molecules per unit volume of gas when $p=1$ and $T=273$.

Then, in the units adopted, since $273\pi N_0\sqrt{(3R/m)}=1.6\times10^{28}$,

$$r=(1.6\times10^{28})A^2p/(1+i)\sqrt{T}; \tag{10}$$

$$\sigma=e^2i/2\pi A^2\sqrt{(3mRT)}=60i/A^2\sqrt{T}; \tag{11}$$

$$K_2=\frac{2\sqrt{3}(273)^2N_0^2e^2\sqrt{R}}{c^3m^{3/2}}\cdot\frac{A^2\lambda^2ip^2,}{T^{3/2}(1+i)^2} \tag{12}$$

$$=(6.9\times10^{26})A^2\lambda^2ip^2/T^{3/2}(1+i)^2;$$

$$K_1=8\pi ne^4/3m^2c^4=(4.9\times10^{-3})ip/T(1+i), \tag{13}$$

since $$8\pi(273)N_0e^4/3m^2c^4=4.9\times10^{-3}.$$

When the mass coefficient of opacity k is employed, K in the above equations is replaced by $k\rho$ where ρ is the density. Thus the mass coefficient of absorption corresponding to K_2 is, for a monatomic gas,

$$k_2=2e^2\lambda^2ri/\pi mc^3M_0W=4.4\lambda^2ri/W \tag{14}$$

$$=(5.7\times10^{28})A^2\lambda^2ip/W(1+i)\sqrt{T},$$

where W is the atomic weight, and M_0 is the mass of the unit of atomic weight, or 1.65×10^{-24}.

In order to apply to physical problems certain of the above equations it is necessary to know the approximate value of A, the collision radius of atoms or ions of the gas. In view of the tentative nature of the theory presented in this paper the determination of A need not be precise. The collision radii of the molecules of the permanent gases at ordinary

temperatures are known to be of the order 10^{-8} cm. The atomic volumes indicate that this is the order of magnitude of the radii of the uncharged atoms of metals. A crude theoretical formula for the collision radii, with regard to electrons, of metallic ions may be derived by the following method.

The ions, each carrying a positive change of average magnitude ie, may be regarded as centers of electrostatic forces which conform to Couloumb's inverse square law. Accordingly, the energy equation of an electron moving in a hyperbolic orbit with velocity u at distance x from an ion is, neglecting the forces due to other ions,

$$\tfrac{1}{2}mu^2=\tfrac{1}{2}mu'^2+ie^2/x,$$

where u' is the velocity at infinity. Assuming equipartition of energy between electrons and other molecules, $mu'^2=3RT$, on the average. It can easily be shown that the distance of closest approach between electron and ion, when the former is deflected through an angle 2θ by the encounter, is $(2ie^2/3RT)\cot^2\theta$. Thus, if θ is taken as $\pi/4$ for the average collision,

$$A=(1.1\times10^{-3})i/T. \tag{15}$$

As the ion is a structure as well as a center of force this value of A is to be regarded only as a rough approximation.

Astrophysical Applications

The opacity of the vapor of an exploded wire. The experiments of Anderson[6] have shown that a layer a few centimeters thick of the vapor of an exploded iron wire is sufficiently opaque to result in the production of a continuous spectrum, and to prevent the transmission of light. In a letter to the writer Dr. Anderson states that his most recent experimental results indicate that the value of K for iron vapor at 20,000° absolute and a total pressure of about 2 atmospheres, is of the order unity (presumably for λ near 4×10^{-5}); and, further, that K varies inversely as λ or λ^2.

The observed spectrum indicates that the iron atoms are for the most part doubly ionized, so that the value of i is about 2. Under these circumstances, (13) gives $K_1=3.3\times10^{-7}$; (10), (11), (12), respectively, give $r=(7.5\times10^{25})A^2$, $\sigma=0.85/A^2$, and $K_2=(3.5\times10^{11})A^2$. The small size of K_1 shows that scattering is not important here.

When $i=2$ and $T=20{,}000$, (15) gives $A=10^{-7}$ cm. Accordingly, $\sigma=8\times10^{13}$ e.s.u./cm^3, a conductivity seven thousand times less than that of metallic copper; and $K_2=0.004$, which is 250 times smaller than

[6] J. A. Anderson, Astrophys. J. **51**, 37, 1920; Proc. Nat. Acad. Sci. **8**, 231, 1922

Anderson's experimental value. If Anderson's published estimate of the pressure, namely $p/(1+i)=20$ atmospheres, is employed, the calculated value of K_2 comes out about 4. Thus, much depends upon the accuracy of the determination of the pressure. Perhaps a more serious disagreement between the theoretical K_2 and the experimentally observed K is that the former varies as λ^2 while the latter, it is thought, varies inversely as λ. Obviously the subject wants further study. The value of the "radius" of the iron ion, especially, is also very uncertain.

Good electrical conductors are good reflectors, as well as good absorbers and emitters of light. If the boundary of the vapor of an exploded wire were sufficiently sharply defined a considerable portion of incident light might be reflected. Thus the "Heaviside layer" of ionized gas in the upper atmosphere of the earth has been supposed by radio engineers to reflect Hertzian waves.

Pressures in the solar atmosphere. The following cursory examination of conditions in the outer regions of the sun indicates that the thermal absorption described by (12) may be an important cause of the opacity of the sun's photosphere.

The temperature of the sun's photosphere and lower reversing layer is not greatly different from 6000°. Substituting in (13) gives

$$10^{-5}/K_1=12(1+i)/ip \tag{16}$$

for the distance in kilometers which would be required to reduce the intensity of the direct beam in the ratio of $1/\epsilon$ if scattering by free electrons were the only cause of opacity.

Ionization in the photosphere may not be sufficiently intense to make (15) applicable; but for purposes of argument A may be assumed as 5×10^{-8}. Then, for $\lambda=6\times10^{-5}$, (12) gives

$$10^{-5}/K_2=(75\times10^{-5})\,(1+i)^2/ip^2 \tag{17}$$

as the distance in kilometers which would be required to reduce the intensity of the direct beam in the ratio of $1/\epsilon$ if the thermal absorption by free electrons were the only cause of opacity.

Saha's well-known theory permits calculation of i, and consequently of $10^{-5}/K_1$ and $10^{-5}/K_2$ in terms of p and T. Table I presents such calculated results for the case of sodium vapor at 6000°. The second ionization of sodium is neglected and Russell's values of i are used.[7] Values of r, the number of collisions per second per electron, are included from (10). This table may be regarded as illustrating, on a simplified scale, conditions in the solar atmosphere. The actual conditions are,

[7] H. N. Russell, Astrophy. J. **55**, 134, 1922

of course, much more complex, and the free electrons which are present have been liberated from all sorts of ions.

TABLE I

The opacity of ionized sodium at 6000°K

Pressure in atmospheres, of sodium vapor and free electrons p	Fraction of ionization i	Collisions per second per electron r	Kilometers distance to reduce intensity to 1/ϵth: Scattering $10^{-5}/K_1$	Absorption $10^{-5}/K_2$
1	0.21	4.2×10^{11}	69	0.0052
10^{-1}	0.56	3.3×10^{10}	330	0.33
10^{-2}	0.90	2.7×10^{9}	2,500	30.
10^{-3}	0.99	2.5×10^{8}	24,000	3000.
10^{-4}	1.00	2.5×10^{7}	240,000	300000.

Table I brings out the predominating influence at moderate and high pressures of thermal absorption by free electrons in producing general opacity, as compared with scattering by free electrons. The latter process is relatively important only at extremely low pressures. It is worth recalling that electromagnetic theory shows that general, as distinct from sharply selective, scattering by bound electrons is not enormously greater (and may be much less) than scattering by free electrons in an appreciably ionized gas.

Since K_2 varies as A^2p^2, a reduction in the estimate of the radius of the sodium ion would increase in the same proportion the values of pressure in the table. In a crystal of sodium chloride the shortest distance between sodium and chlorine ions is known to be 2.8×10^{-8} cm. It seems unlikely that the collision radius of the sodium ion should be much less than half this. If thermal absorption by free electrons in the solar atmosphere really is as intense as the numbers in the last column of Table I indicate, it is at once apparent that at a depth where the pressure is as great as 0.01 atmosphere the opacity is sufficient to cut off light from lower levels. This figure, then, is indicated as an upper limit to the pressure in the visible regions in the solar atmosphere. Photospheric absorption may be supposed to set in at, or above, this depth.

When observations are made of the flash spectrum, the grazing line of sight runs for tens of thousands of kilometers through the solar atmosphere. The faintness of the continuous spectrum under these conditions indicates, in connection with Table I, a pressure of less than 0.001 atmosphere at these levels. A detailed examination of the conditions is outside the province of the present paper. Other lines of evidence, for example the sharpness of the Fraunhofer lines, indicate that the pressures are very low.

The opacity deep in stars. In his well-known theoretical study of conditions in the interior of stars Eddington[8] has found that the mass absorption coefficient has a value of the order 20. Recently he has dealt with this matter by a kind of quantum theory.[9]

It is of interest to consider the application of (14) to conditions in the interior of stars. If the wave-length considered is that of maximum energy radiation, the value of λ to be substituted in (14) is $\lambda = 0.29/T$. Making use also of (15),

$$k_2 = (5.8 \times 10^{22}) i^3 p / W T^{9/2} (1+i). \tag{18}$$

By Eddington's theory of stellar constitution,

$$(1.0 \times 10^6) p = \beta a T^4 / 3(1+\beta), \tag{19}$$

where a is Stefan's constant, or 7.6×10^{-15}, and the factor 1.0×10^6 is approximately the number of c.g.s. units of pressure in one atmosphere. For purposes of illustration the value of β may be taken as 0.83, which makes (19) apply to a giant star of mass 1.5 times that of the sun. Substituting in (18),

$$k_2 = 700 i^3 / W(1+i)\sqrt{T}.$$

Since by definition there are i free electrons for every atom, W may be written as $W'/(1+i)$, where W' is the average molecular weight of the positive ions. Accordingly,

$$k_2 = 700 i^3 / W' \sqrt{T} = 30 i^3 / \sqrt{T}, \tag{20}$$

if W' is 23.

At the center of the star, T is of the order 4×10^6, and i may be taken as 12, say. Thus k_2 at the center is given as 25. Near the surface, say, where T is 10,000 and i is 2, k_2 is given as 2.4 Thus the opacity described by (20) is of the order of magnitude of the Eddington opacity, and also is roughly consistent with Eddington's original assumption that k does not vary with depth in the star.

In conclusion, the tentative character of the results presented scarcely needs to be emphasized. The subject of the opacity of gases to radiation is a broad and important one, which can be approached from many angles. In dealing with it the possibilities of classical electromagnetic theory appear by no means to have been exhausted.

I wish to thank Professor Russell for his very helpful interest in the preparation of this paper.

PRINCETON UNIVERSITY OBSERVATORY,
March 7, 1923.[10]

[8] A. S. Eddington, Astrophys. J. **48**, 212, 1918
[9] A. S. Eddington, Monthly Notices, **83**, pp. 32, 98, 1923
[10] Received April 16, 1923

ON THE MOTIONS OF ELECTRONS IN GASES

By K. T. Compton

Abstract

Motion of electrons through gases when electric field and pressure are such that collisions are elastic.—For electron speeds below a critical value characteristic of each gas, the collisions with molecules are probably as between elastic spheres, since neither ionization nor radiation is produced. The average fraction of its *energy lost in elastic collision* with a molecule of mass M, by an electron of mass m, is $f=2(m/M)(1-\Omega/U)$, where Ω and U are the average kinetic energies of molecules and electrons. But while, if $U>\Omega$, the electrons lose energy at collisions, they gain energy from the field between collisions, so the kinetic energy tends to increase or decrease to a *terminal energy*. Assuming Langevin's equation for mobility, we find U_t (in volts) $=.66\ El/\sqrt{f}$ where El is the product of field strength and mean free path. In the case of plane parallel electrodes the number of collisions per cm and also the ratio of the speed at any point to the terminal speed, are both found to be independent of the field strength. In the case of a straight filament cathode surrounded by a coaxial cylindrical anode, the electrons may acquire their maximum speed near the cathode and subsequently lose speed while approaching the anode, their speed being greater than the terminal speed for this region. Curves are given for various cases. Substituting the value of terminal speed in Langevin's equation leads to the following expression for *electron mobility:* $\mu=0.815l\sqrt{(\frac{1}{2}e/m)}/[\frac{1}{2}\Omega+(\Omega^2/4+W^2)^{\frac{1}{2}}]^{\frac{1}{2}}$ where the energy due to the field is $eW=leE/1.506\sqrt{f}$. This expression is somewhat similar to that given by Loeb (corrected for numerical error) but leads to values 0 to 10 per cent higher. When the collisions are inelastic the mobility is shown to be greater.

TO a certain degree of approximation, which varies with conditions, collisions of electrons with gas molecules may be regarded as if between elastic spheres, provided the relative velocities do not exceed a value characteristic of the particular gas. The motions of such electrons in gases may then be treated by the ordinary methods of the Kinetic Theory of Gases. For many practical purposes such a treatment is sufficiently accurate. In this paper are presented some characteristics of electron motions in a gas in an electric field, with some applications to experimental results and a discussion of the conditions in which the method is inapplicable. We shall consider principally cases in which the gas pressure is sufficiently large, in comparison with the electric field, to make the average speed gained between successive collisions small compared with the total speed.

Consider first electrons each of charge e, mass m, speed $\bar{v}$, moving with a mean free path l in a gas under the influence of an electric field E.

If the speed gained between successive collisions is small compared with the total speed $\bar{v}$, all directions of motion are statistically equally probable after an impact and the average distance advanced during each interval between collisions is

$$s = \tfrac{1}{2}a\bar{t}^2 = \tfrac{1}{2}(eE/m)\ (l/\bar{v})^2,$$

where $a = eE/m$ is the acceleration and $l/\bar{v}$ is the mean free time $\bar{t}$.

The mean rate of advance of the electrons, which may be written as the mobility μ multiplied by the electric field E, is

$$\mu E = s/t = \tfrac{1}{2}eEl/m\bar{v}.$$

Hence the electron mobility is

$$\mu = \tfrac{1}{2}el/m\bar{v}.$$

This simple relation is inaccurate for several reasons. The effect of a distribution of free paths and of speeds cannot be averaged simply by use of average values of paths and speeds, and the dynamical effect of the collisions is such as to make the average initial speed after a collision different from zero. Townsend[1] gives an approximate treatment of the kinematical correction, which is more thoroughly treated by Lorentz;[2] Maxwell[3] considered the dynamical correction but not the complete kinematical one, while Langevin[4] and Lenard[5] considered both. Langevin's equation for μ may be written

$$\mu = \frac{3\sqrt{(3\pi)}}{8\sqrt{2}}\frac{el}{mc}\sqrt{\frac{m+M}{M}}, \tag{1}$$

where c is the square root of the mean square speed and M is the mass of a molecule. A critical discussion of these equations is given by Mayer.[6]

Boltzmann[7] and Langevin showed that the electrons acquire a Maxwell's distribution of speeds about their mean velocity of drift, so that $c = 1.086\ \bar{v}$. Since m is very small compared with M, we may write (1)

$$\mu = 0.75\ el/m\bar{v}, \tag{2}$$

in which the factor 0.75 differs from that quoted by Townsend, 0.815, because of our substitution of $\bar{v}$ for c.

Pidduck[8] has recently shown that the electrons do not acquire exactly a Maxwell distribution of speeds, and that the departure from such a distribution may increase the numerical factor by about eleven per cent.

[1] Townsend, Electricity in Gases, p. 83
[2] Lorentz, Theory of Electrons, p. 68
[3] Maxwell, Scientific Papers, **1**, 398, 1890
[4] Langevin, Ann. de Chim. et de Phys., (8), **5**, 245, 1905
[5] Lenard, Ann. der Phys. **60**, 329, 1920
[6] Mayer, Jahr. Radioakt. Elek. **18**, 201, 1922
[7] Boltzmann, Gastheorie, vol. 1, p. 114
[8] Pidduck, Proc. London Math. Soc. **15**, 89, 1916

In the following treatment, we shall neglect this departure and assume the correctness of equations (1) and (2).

Since μE is the average distance advanced in the direction of the electric field in a second, and $\bar{v}/l$ is the average number of collisions made during the same time,

$$s = l\mu E/\bar{v} = 0.75\ l^2 eE/m\bar{v}^2 \tag{3}$$

is the average advance between successive collisions. If we put $\bar{v}^2 = 0.849\ c^2$, as in a Maxwell's distribution, and $eU = \frac{1}{2}mc^2$, we obtain

$$s = 0.441\ l^2 E/U. \tag{4}$$

Thus the average number of collisions $1/s$ made while advancing unit distance varies inversely as l^2 and hence directly as the square of the gas pressure p.

If ν is the number of electrons per unit volume, the current density j of electrons is

$$j = \nu e\mu E = 0.75 le^2 E\nu/m\bar{v} \tag{5}$$

and the density of negative space charge ρ is

$$\rho = \nu e = jm\bar{v}/0.75\ leE. \tag{6}$$

Number of Collisions made while Advancing a Distance from the Cathode

Consider first electrons emitted with negligible speed from a plane cathode and drawn through a gas toward a plane parallel anode. The total average number of collisions per electron in distance d is

$$N = \int_0^d \frac{1}{s}\,dx = \int_0^d \frac{Ex\,dx}{0.441\ l^2 E} = 1.134\,\frac{d^2}{l^2}. \tag{7}$$

This differs by the factor 1.134 from a similar expression derived by Hertz.[9]

If the electrons are emitted from a cylinder of radius r_c, such as a wire filament, and are drawn toward a coaxial cylindrical anode, the average number of collisions made by an electron while attaining a distance r from the axis is

$$N = \int_{r_c}^{r} \frac{U}{0.441 l^2 E}\,dr = \int_{r_c}^{r} \frac{r}{0.441 l^2} \log\frac{r}{r_c}\,dr$$

since, if σ is the charge per unit length of the cathode, $E = 2\sigma/r$ and $U = \int E dr = 2\sigma \log r/r_c$. This integral gives

$$N = 1.134\frac{r^2}{l^2}\left\{\log\frac{r}{r_c} - \tfrac{1}{2} + \tfrac{1}{2}\frac{r_c^2}{r^2}\right\}. \tag{8}$$

[9] Hertz, Physics, 2, 15, 1922

This reduces, of course, to Eq. (7) if $r=r_c+d$, where d is small compared with r_c, i.e., when the distance from the cathode is so small compared with its radius that it can be considered as a plane surface.

Eqs. (7) and (8) are inaccurate in that they assume no loss of energy by the electrons as they advance through the field. Such losses actually exist, for even if the collisions are perfectly elastic, some momentum is transferred to the molecules at each impact. At high gas pressures these energy losses, though individually very small, are in the aggregate quite large and limit the speed which the electrons attain in any given field. The consequences of these energy losses are considered in the following two sections.

Energy Losses at Collisions

If an electron collides with a molecule, initially at rest, and is thereby deflected through an angle φ with a change in speed from v to v_1, the molecule receives a velocity ω_1 in the direction θ. Assuming perfect elasticity (as for electron impacts below the critical speed for inelastic impacts) we have the relations

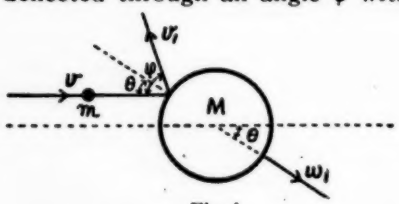


Fig. 1

$$mv+mv_1\cos\varphi=M\omega_1\cos\theta$$
$$mv_1\sin\varphi=M\omega_1\sin\theta$$
$$\tfrac{1}{2}mv^2-\tfrac{1}{2}mv_1^2=\tfrac{1}{2}M\omega_1^2,$$

from which

$$f_\theta=\frac{\tfrac{1}{2}mv^2-\tfrac{1}{2}mv_1^2}{\tfrac{1}{2}mv^2}=4\frac{Mm}{(M+m)^2}\cos^2\theta$$

gives the fraction of its energy lost by the electron at the collision. Actually electrons may strike the molecule at any angle θ between 0 and $\pi/2$, and the average fraction of the energy lost is

$$f=\frac{1}{\pi}\int_0^{\pi/2} f_\theta\, 2\pi\sin\theta\cos\theta\, d\theta=2\frac{Mm}{(M+m)^2}.$$

Since M is much larger than m, we may put

$$f=2m/M. \tag{9}$$

We have assumed, thus far, that the molecules are initially at rest. We may take into account the effect of initial molecular velocities by averaging the effects of two types of collisions, between electrons and molecules moving in opposite directions with average speeds c and ω and between those moving in the same direction. Out of N collisions,

there are $\frac{1}{2}N(c+\omega)/c$ of the first type, resulting in an average energy loss equal to $M[(m/M)^2c^2+(m/M)c\omega]$, and $\frac{1}{2}N(c-\omega)/c$ collisions of the second type, with an average energy loss equal to $M[(m/M)^2c^2-(m/M)c\omega]$. We can therefore obtain the total loss of energy by the electrons in all N collisions, and thus the average loss per collision. When this is divided by the average energy before collision we obtain.[10]

$$f=2\left(\frac{m}{M}-\frac{\omega^2}{c^2}\right)=2\frac{m}{M}\left(1-\frac{\Omega}{U}\right). \tag{10}$$

If the speed c of the electrons is less than that which would make them in thermal equilibrium with the gas, f is negative and the electrons gain energy at encounters, on the average. If, as is the case in an electric field, their mean kinetic energy exceeds that of the gas molecules, they lose energy at collisions. Eq. (9) may be used with sufficient accuracy except under conditions, such as high gas pressures and small fields, in which the mean energy of the electrons is not much greater than that of the molecules.

Eq. (9) has been experimentally verified for helium and it is shown in a later paper that it is probably true for impacts in nitrogen and hydrogen. We may assume it to be correct for impacts of electrons with monatomic molecules at speeds below their minimum radiating speeds, and for at least some multiatomic molecules under similar conditions.

Terminal Speeds

In advancing a distance dx in a field E each electron gains energy $eEdx$, and loses an average of feU at each of the dx/s intervening collisions. The net gain of energy per electron is

$$edU=e(E-fU/s)dx.$$

Substituting for f and s from (10) and (4), we have

$$dU/dx=E-4.536\,mU(U-\Omega)/l^2ME. \tag{11}$$

The terminal speed of steady drift is found by solving this equation for U when $dU/dx=0$, giving

$$U_l=\tfrac{1}{2}\Omega+\sqrt{\frac{\Omega^2}{4}+\frac{l^2ME^2}{4.536m}} \tag{12}$$

in equivalent potential drop. In terms of average speed, since $\frac{1}{2}mc^2=eU$ and $c=1.086\bar{v}$, and the mean energy $e\Omega$ of the molecules is given in terms of absolute temperature by αT,

$$\bar{v}_l=\frac{1}{1.086\sqrt{m}}\left[\alpha T+\left(\alpha^2T^2+\frac{l^2ME^2e^2}{1.134\,m}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}. \tag{13}$$

[10] Benade and Compton, Phys. Rev. ~~9, 187, 1918~~ 11, 184, 1918

In most practical cases, Ω or aT are so small compared with the other terms that they can be neglected. This is equivalent to using Eq. (9) in place of Eq. (10) for f. In such cases Eqs. (12) and (13) for terminal speed reduce to

$$U_t = \frac{lE}{2.13}\sqrt{\frac{M}{m}} \tag{14}$$

$$\bar{v}_t = 0.891\left(\frac{lEe}{m}\sqrt{\frac{M}{m}}\right)^{\frac{1}{2}}. \tag{15}$$

We may obtain an approximate idea of the magnitudes of these terminal speeds under various conditions by putting the mean free path $l = 4\sqrt{2}\cdot L$, where L is the mean free path of a gas molecule. This relation is known to be approximately correct, although there are deviations from it, which will be discussed in a later paper. From Table I the terminal energies in equivalent volts may easily be computed for various fields and gas pressures in the case of some common gases.

TABLE I

Terminal energies in various gases

l_1 = electronic free path at 1 mm pressure and 20°C.
$U_t = A\,E/p$, where E is in volts/cm and p in mm.

Gas	$\sqrt{(M/m)}$	l_1(cm)	U_t(volts)
He	85.9	.1313	$5.30\,E/p$
A	271.5	.0461	5.86
H_2	60.8	.0842	2.40
N_2	227.4	.0435	4.65
CO_2	285.0	.0290	3.88
Hg	608.0	.0135	3.85

These values of U_t are meaningless (1) if E and p are so chosen as to make U_t comparable with the mean energy of thermal agitation $\Omega = 0.0372$ volts, in which case Eq. (12) must be used in place of Eq. (14); (2) if E and p are so chosen as to make U_t comparable with the critical energy at which electron impacts become inelastic. Between these values Table I should be approximately correct.

When in this terminal state of speed, the average number of collisions made per centimeter advance is given by Eqs. (4) and (14) as

$$\frac{1}{s} = \frac{1.565}{l}\sqrt{\frac{M}{m}}. \tag{16}$$

MEAN ENERGY OF ELECTRONS AT ANY DISTANCE FROM CATHODE

(a) *Plane parallel electrodes.* The rate of gain of energy at any point is given by Eq. (11). Putting

$$4.536\, m/l^2M = 4.536\, p^2m/l_1^2M = a^2 \tag{17}$$

and integrating from $U=0$ at the cathode $x=0$ to $U=U$ at the distance $x=x$ from the cathode, we find the mean energy at distance x to be

$$U=\tfrac{1}{2}\Omega+E\sqrt{\frac{1}{a^2}+\frac{\Omega^2}{4E^2}}\,\frac{\epsilon^{2a^2\sqrt{(1/a^2+\Omega^2x/4E^2)}}-1}{\epsilon^{2a^2\sqrt{(1/a^2+\Omega^2x/4E^2)}}+1}. \tag{18}$$

If the field $E=0$, this reduces to $U=\Omega$, i.e., the energy of the electrons is simply that of thermal agitation. If the energy due to the field is so large that Ω may be neglected, Eq. (18) becomes

$$U=\frac{E}{a}\,\frac{\epsilon^{2ax}-1}{\epsilon^{2ax}+1} \tag{19}$$

which is identical, except for a small correction in the value of a, with an equation previously derived.[11] When x is very large, U approaches the terminal value $U_t=E/a$, which is identical with Eq. (14).

The mean energies of the electrons at any distance from the cathode for various values of field and gas pressure with different gases are shown in Figs. 2 and 3. Fig. 2 gives U as a function of x for various fields and values of a, and Fig. 3 indicates the type of gas and its pressure corresponding to any value of a.

The average number of collisions made while going a distance x from the cathode is given by (4) as

$$N=\int_0^x\frac{1}{s}\,dx=\int_0^x\frac{U}{0.441\,l^2E}\,dx.$$

If we substitute for U from Eq. (18) and integrate we obtain the correct number of collisions. If we substitute from Eq. (19) we get a number which is quite accurate except in very weak fields. From Eq. (19) we find readily that

$$N=(M/4m)\,[\log\,(2+\epsilon^{2ax}+\epsilon^{-2ax})-\log 4]. \tag{20}$$

This equation reduces to $N=0$ if $x=0$. If x is very large N approaches x times the value of $1/s$ given by Eq. (16) for the case of terminal speed. If energy losses are negligible, which means M/m has a very large value, N takes the value given in Eq. (7).

From Eq. (19) we can readily compute the distance d in which the electrons acquire a fraction φ of their terminal energy to be

$$d=\frac{1}{2a}\log\frac{1+\varphi}{1-\varphi}, \tag{21}$$

and the average number of collisions made while acquiring this fraction of the terminal energy is

$$N=\frac{M}{4m}\log\frac{1}{1-\varphi^2}. \tag{22}$$

[11] Benade and Compton, loc. cit.[10]

Similarly, the average time to go a given distance or acquire a given fraction of the terminal energy may easily be computed from these equations. It is interesting that the number of collisions made in any given

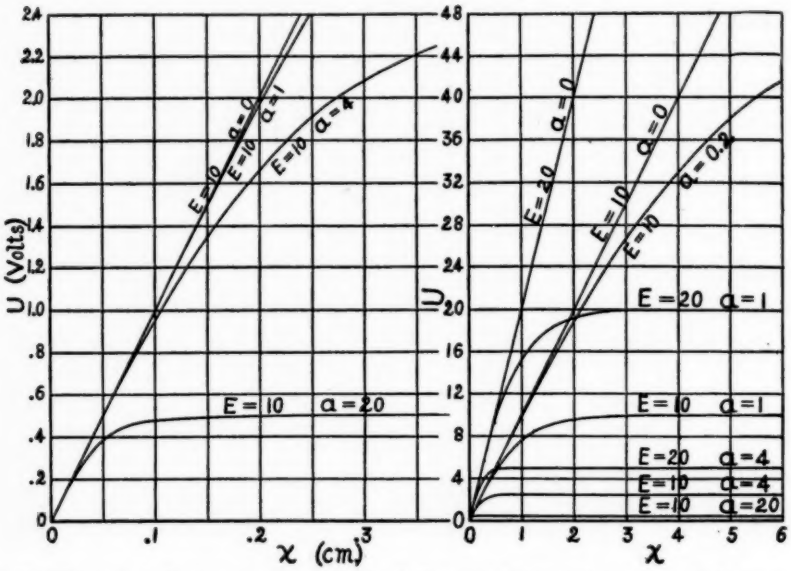


Fig. 2. Energy of electrons as a function of distance from a plane cathode for certain values of the field E and pressure factor a.

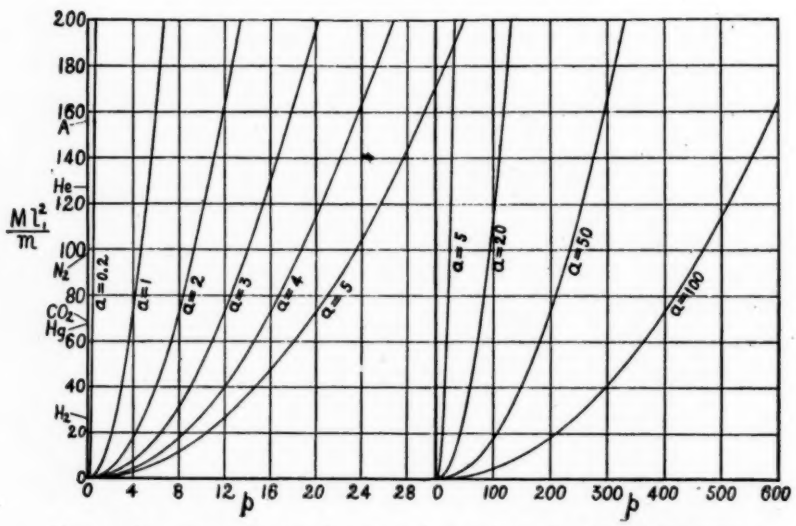


Fig. 3. Pressures corresponding to various values of a for various gases.

distance is independent of the strength of field; the distance in which a fraction φ of the terminal energy is acquired is independent of the field;

and the number of collisions made while acquiring any fraction of the terminal energy is independent of both the field strength and the mean free path.

The terminal speeds are acquired surprisingly quickly in gases at considerable pressure, as illustrated in Table II.

TABLE II

Distance in which fraction φ of terminal energy is acquired (0°C)

p	φ	Helium d (cm)	Nitrogen d (cm)	Mercury d (cm)
760	0.1	0.00064	0.00057	0.00047
	0.2	0.00131	0.00115	0.00096
	0.5	0.00356	0.00313	0.00262
	0.9	0.00953	0.00840	0.00708
	0.99	0.01710	0.01507	0.01260
10	0.1	0.049	0.043	0.036
	0.9	0.724	0.638	0.533
1	0.1	0.49	0.43	0.360
	0.9	7.24	6.38	5.33

(b) *Coaxial cylindrical electrodes.* This case is of particular interest because it corresponds to the common arrangement of a hot wire filament source of electrons situated at the axis of a surrounding cylindrical anode.

The rate of gain of energy by an electron at any point between the electrodes is given by Eq. (11), with

$$E=2\sigma/r \text{ and } 2\sigma=(V_a-V_c)/\log\,(r_a/r_c), \tag{23}$$

where V_a, V_c and r_a, r_c are the potentials and radii of the anode and cathode, respectively. Introducing a from Eq. (17), we have

$$\frac{dU}{dr}=\frac{2\sigma}{r}+\frac{a^2\Omega\bar{U}r-a^2U^2r}{2\sigma}. \tag{24}$$

I have been unable to find a solution of this equation, but have evaluated the integral by a laborious step-by-step process, as follows.

If r_1 and r_2 are very nearly equal, we may consider the field in the interval r_2-r_1, to be constant and given by $E=\sqrt{(E_1E_2)}$ and calculated from Eqs. (23) in terms of the applied potential difference and the dimensions of the electrodes. We may then use

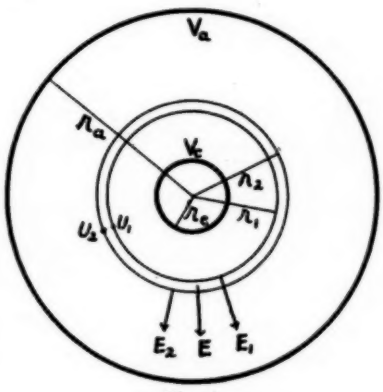


Fig. 4

$$dU/dr=(E^2+a^2\Omega U-a^2U^2)/E$$

and integrate to find the increase in U through this range from r_1 to r_2

$$\int_{U_1}^{U_2}\frac{dU}{E^2+a^2\Omega U-a^2U^2}=\int_{r_1}^{r_2}\frac{dr}{E}.$$

I have solved the special case where the term in Ω is negligible, as is the case when electron energies are larger than about 0.05 of the minimum ionizing energy of any gas. We then find the mean energy U_2 at the end of the interval in terms of the energy U_1 at the beginning of the interval to be

$$U_2=\frac{E(E+aU_1)\epsilon^{-2a(r_2-r_1)}-(E-aU_1)}{a(E+aU_1)\epsilon^{-2a(r_2-r_1)}+(E+aU_1)}. \tag{25}$$

This process may be carried out over each of the small intervals into which

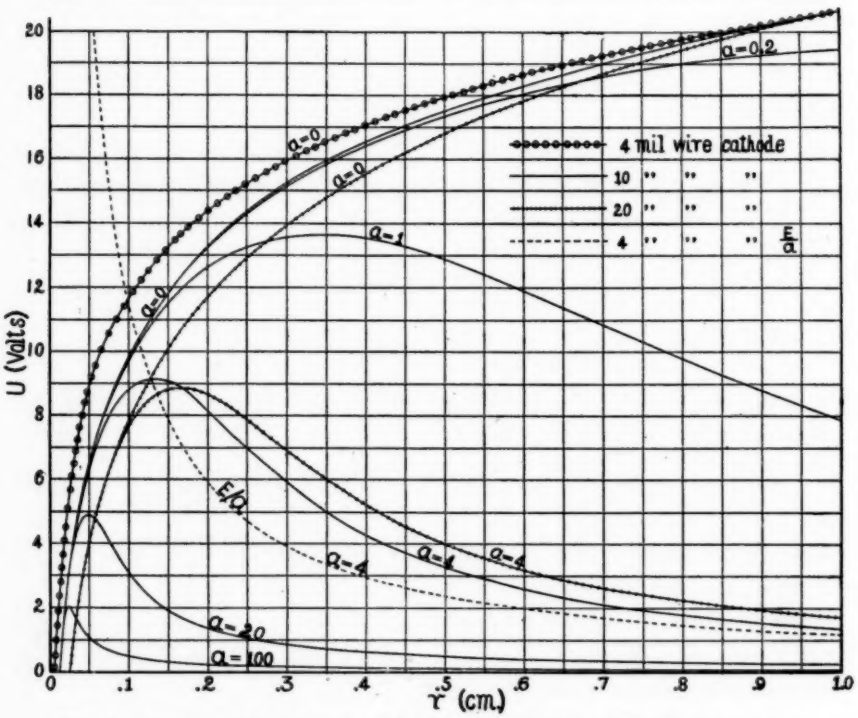


Fig. 5. Energy of electrons at various points between cylindrical electrodes.

the space between the electrodes is subdivided, and the energy at every point thus determined.

Examples of the way in which electrons gain energy between cylindrical electrodes in gases are given in Fig. 5. The gas pressure for any type of gas corresponding to each value of a may be found in Fig. 3. The

curves are drawn for cases of 4, 10 and 20 mil wires ($r_c = 0.005$, 0.0125, 0.0250 cm, respectively) with an anode of 1 cm radius and an applied potential difference $V_a - V_c = 20.66$ volts. The same curves may be made to apply to other cases by altering the units according to the relations shown in Eq. (23).

It is seen that even at quite moderate gas pressures, as low as 1 mm, the aggregate loss of energy at impacts is quite large and the electrons fail to acquire the energy corresponding to the applied potential difference. At the higher pressures the electrons acquire their greatest energy quite close to the filament, and lose energy as they proceed toward the anode into the regions of less electric intensity. The maximum value of U for each curve is that which is equal to the terminal speed for the electric intensity at that particular point, as given by $U = E/a$, by Eq. (14). To the left of this maximum the electrons have less energy than the terminal value corresponding to their location, while to the right they have greater energy than the corresponding terminal value. This is illustrated by the curve of theoretical terminal energy drawn for one particular case ($a = 4$).

These facts have a bearing on the design of ionization tubes for work at low voltages. For instance, the theory of cumulative ionization[12] indicates that the effect of imprisoned resonance radiation in promoting ionization should increase with increase of gas pressure and thus an increase of gas pressure should facilitate the striking of a low voltage arc. This is true up to about 5 mm (depending on the electrode distance), but above this pressure the arc strikes with increasing difficulty and higher voltage is required. This is to be expected in view of the large energy loss by impacts at the higher pressures.

Since, at these gas pressures, the electrons have approximately a Maxwell's distribution of speeds, some may ionize even though the mean energy is below the minimum ionizing energy. The greater part of the ionization will occur in the region of the maximum value of U.

The above considerations still hold in principle, but the equations and numerical values must be altered, if the electron current density is so great as to appreciably alter the potential distribution between the electrodes. In the case of a large current from a filament, for instance, the negative space charge shifts the regions of large electric intensity toward the anode, so that curves like those in Fig. 5 would reach a lower maximum value of U and this maximum would be shifted toward the anode. The correct curves giving the mean energy at every point

[12] Compton, Phys. Rev. **20**, 283, 1922; Phil. Mag. **45**, 1923

could be obtained by the method of Eq. (25) if the actual distribution of potential between the electrodes were known.

Electron Mobilities in Gases

The electron mobility in electric fields is given by Eq. (2) provided the mean speed $\bar{v}$ is so small that there are no appreciable number of ionizing or otherwise inelastic impacts. (According to Pidduck[8] the numerical factor may be as large as 0.84.) Substitution for the average speed from Eq. (13) gives, for the mobility,

$$\mu = \frac{0.815 el}{\sqrt{m}[\alpha T + (\alpha^2 T^2 + l^2 M E^2 e^2/1.134m)^{\frac{1}{2}}]^{\frac{1}{2}}}. \tag{26}$$

If the speed due to the field is negligible compared with that due to thermal agitation, this equation reduces to the familiar mobility equation[13]

$$\mu_0 = 0.815\ el/\sqrt{(2m\alpha T)} = 0.815\ el/mc_0 = 0.75\ el/m\bar{v}_0. \tag{27}$$

If, on the other hand, the ratio E/p is so large that the speed of thermal agitation is negligible compared with that due to the field,

$$\mu_1 = 0.842\sqrt{\frac{el}{E\sqrt{(Mm)}}} = 0.707\sqrt{\frac{el\sqrt{f}}{Em}}. \tag{28}$$

When E/p is small, the mobility is therefore independent of the field; when E/p is large, the mobility decreases as the field increases. The mobility is evidently greater the less elastic are the collisions, as is shown by the presence of the quantity f in the numerator of Eq. (28). In terms of f, the complete mobility Eq. (26) takes the form

$$\mu = \frac{0.815\ el}{\sqrt{m}[\alpha T + (\alpha^2 T^2 + 1.76\, l^2 E^2 e^2/f)^{\frac{1}{2}}]^{\frac{1}{2}}}. \tag{29}$$

The so-called "mobility constant" K, is defined as the mobility of electrons in the gas at 760 mm pressure and 0°C, and is given by

$$K = (p/760)\ (273/T)\mu. \tag{30}$$

Loeb[14] was the first to derive a mobility equation in which the effect of both thermal agitation and the electric field were considered in estimating the mean velocity of drift to be substituted in Eq. (2). His equation, when expressed in the symbols of the present paper, is

$$\mu' = \frac{0.815\ el}{\sqrt{m}[2\alpha T + 0.575\, lEe/\sqrt{f}]^{\frac{1}{2}}}. \tag{31}$$

The difference between Loeb's equation and Eq. (29) may be seen most easily by putting $\alpha T = e\Omega$ and $lEe/1.506\sqrt{f} = eW$, where $e\Omega$ is the energy of thermal agitation and eW is the energy which the electrons would have

[13] Townsend, Phil. Mag. **40**, 505, 1920
[14] Loeb, Phys. Rev. **19**, 24, 1922

acquired from the field had the thermal energy of the molecules not been contributed. In this notation Eqs. (29) and (31) take the forms

$$\mu = \frac{0.815\, el}{\sqrt{(2me)[\frac{1}{2}\Omega+(\Omega^2/4+W^2)^{\frac{1}{2}}]}}, \tag{29a}$$

$$\mu' = \frac{0.815\, el}{\sqrt{(2me)[\Omega+0.433\, W]}}. \tag{31a}$$

The presence of the factor 0.433 in Loeb's equation is due (1) to his use of a value of the terminal energy which I derived in an earlier paper[15] and which is less accurate than the value used in the present paper and (2) to his use of this energy as a maximum rather than a mean value, thereby erroneously dividing it by 2.

Apart from this numerical inaccuracy, which is accidental, the two expressions differ in form. Loeb takes the resultant terminal energy of electrons to be the sum of the energies which would be due to thermal agitation and to the field if each agency contributed additively. Thus his term in brackets, after correcting the numerical error, is $U'=\Omega+W$ whereas the correct value is

$$U=\tfrac{1}{2}\Omega+(\Omega^2/4+W^2)^{\frac{1}{2}} \tag{32}$$

If we put k equal to the ratio of the actual energy U to the energy of thermal agitation Ω, we have from (32)

$$U=k\Omega, \qquad W/\Omega=\sqrt{[k(k-1)]}, \tag{33}$$

whereas on Loeb's assumption we would have

$$U'=k'\Omega, \qquad W/\Omega=k'-1, \tag{34}$$

which is the same as an equation derived as an approximation by Pidduck and frequently used by Townsend.[16]

It is found that the equations of Loeb and Pidduck are correct at both extremes, when $k=1$ and when $k=\infty$, but that there is a small error at intermediate values, reaching its maximum at $k=4/3$, when $W=(2/3)\Omega$. Here k' is 25 per cent larger than the true value k, and the mobility μ' calculated by Loeb's corrected equation is about 10 per cent less than the theoretical value μ. It is likely that some of the conclusions regarding small departures from perfect elasticity of electron impacts in gases, which Townsend has based on Eq. (34), should be reconsidered in the light of Eq. (33).

Special Case of Completely Inelastic Impacts

This case cannot be considered as a special case of elastic impacts, using Eq. (31) with $f=1$, since that equation was derived on the assump-

[15] Benade and Compton, loc. cit.[10]

[16] It should be noted that we have used the symbols W and Ω as energies, whereas Pidduck and Townsend use them as speeds, so that they appear squared in their equation corresponding to (34).

tion that the speed gained between impacts is small compared with the mean speed. In the case of perfectly inelastic impacts we assume that the electron starts from rest after each encounter. The mean speed of advance is easily found as follows.

Consider the N electrons which cross the plane $x=0$ in any long interval of time. Ndx/l of these collided previously in the layer between x and $x+dx$. Of these, the fraction $\epsilon^{-x/l}$ has arrived at the plane without making an intervening collision. Thus $(N/l)\epsilon^{-x/l}dx$ electrons arrive directly from distances between x and $x+dx$. Their kinetic energy is $\frac{1}{2}mv^2=Eex$, whence $x=mv^2/2Ee$ and $dx=(mv/Ee)dv$. Substituting above, we have

$$F(v)dv=(mv/lEe)\epsilon^{-(mv^2/2lEe)}dv \tag{35}$$

as the fraction which arrives with speeds between v and $v+dv$. The average speed is

$$\bar{v}=\int_0^\infty v\ F(v)\ dv=\sqrt{\frac{\pi}{2}\frac{lEe}{m}}. \tag{36}$$

The mobility is $\mu=\bar{v}/E$, or

$$\mu=\sqrt{\frac{\pi}{2}\frac{le}{mE}}. \tag{37}$$

It is readily seen that the mobility in these circumstances is considerably greater than it would be if the impacts were elastic. Probably impacts in all gases are elastic below critical velocities characteristic of each gas. These critical velocities are known to be much higher than the mean thermal velocity in most cases, although there are probably some gases in which electron impacts are inelastic at speeds below ordinary speeds of thermal agitation.

A test and discussion of these mobility equations will be presented shortly in another paper.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
May 1, 1923.

CURRENTS LIMITED BY SPACE CHARGE BETWEEN COAXIAL CYLINDERS

By Irving Langmuir and Katharine B. Blodgett

Abstract

Limiting current between coaxial cylinders; calculation of the function $\beta=f(r/r_0)$ in the space charge equation $i=(2\sqrt{2}/9)\sqrt{(e/m)}\,V^{3/2}/(r\beta^2)$. Two different infinite series were obtained for β and the coefficients for fourteen terms of each were determined. These two sets were checked against each other. Thus values of β^2 were obtained accurate to 1 in 10,000. These were checked by an integration method which was also used to calculate values in the region where the series failed. For a cathode of radius r_0 inside an anode of radius r, β^2 increases from 1 at $r/r_0=11.2$ to a maximum value 1.0946 at $r/r_0=42$, decreases to a minimum value 0.9990 at $r/r_0=30{,}000$, and becomes 1 at $r/r_0=\infty$. The customary assumption $\beta^2=1$ has therefore led to errors up to 9.5 per cent in previous calculations, but this error is usually about equal and opposite to that introduced by neglecting the effect of initial velocities. For the cathode outside the anode, β^2 is given very closely by the equation $\beta^2=4.6712\ (r_0/r)\ [\log_{10}(r_0/r)-\log_{10}\sqrt{2}]^{3/2}$, for $r_0/r>10$. The empirical constant $\sqrt{2}$ is interpreted to mean that the potential distribution near the anode is unaltered if the hot cathode is replaced by a cold cylinder having one half the cross-section of the original cathode. The correction for initial velocities is less for a cylindrical cathode inside an anode than for parallel planes. In the inverted case it is much greater than in the case for parallel planes, and the effect of the tangential component of the initial velocity may greatly decrease the current that flows.

IN PREVIOUS papers[1] it has been shown that in a very high vacuum the space charge of the electrons limits the current that can flow from a hot cathode to a positively charged anode so that beyond a certain point an increase in the temperature of the cathode causes no further increase in current. When the cathode and anode are long coaxial cylinders the current limited by space charge is given by

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{(r\beta^2)} \tag{1}$$

Here i is the electron current per unit length along the axis, V the voltage at any point P, r the radius at P, e and m the charge and mass respectively of an electron.

Expressing i, r, and V in amperes per cm, cm, and volts, respectively, the equation becomes

$$i=14.68\times10^{-6}V^{3/2}/(r\beta^2) \tag{1a}$$

[1] Langmuir, Phys. Rev. **2**, 450, 1913; Phys. Zeits. **15**, 348, 1914

$\beta = f(r/r_0)$ is a quantity of zero dimensions, r_0 being the radius of the cathode. Values for β^2 were given in a short table, but these were derived from a rough method of calculation and many of them have an error of several per cent. The object of the present paper is to correct and extend this table and to give values of β for the inverted case where the cathode is the outside cylinder.

It was shown in the derivation of Eq. (1) that

$$r(d^2V/dr^2)+dV/dr = i\sqrt{\frac{2m}{eV}} \tag{2}$$

Substitution of Eq. (1) in Eq. (2) gives

$$3\beta r^2(d^2\beta/dr^2)+r^2(d\beta/dr)^2+7\beta r(d\beta/dr)+\beta^2-1=0 \tag{3}$$

Placing

$$\gamma = \log\,(r/r_0) \tag{4}$$

we obtain

$$3\beta(d^2\beta/d\gamma^2)+(d\beta/d\gamma)^2+4\beta(d\beta/d\gamma)+\beta^2-1=0 \tag{5}$$

The solution of this equation gives the series[2]

$$\beta = \gamma-(2/5)\gamma^2+(11/120)\gamma^3-(47/3300)\gamma^4+ \ldots . \tag{6}$$

This was the series used to calculate β^2 but is accurate only for small values of γ. The values obtained are all too low, the error at $r/r_0=5$ amounting to $-.011$.

The value $\beta=1$ is a solution of Eq. (3) and corresponds to the case that $r/r_0=\infty$. A second method[3] for calculating β was based on a substitution

$$\beta = 1-\epsilon^{-\mu}$$

and a series was obtained for μ. The values of β obtained in this way converged so rapidly to unity for $r/r_0=11$ to 20 that the accuracy of the method was held to be doubtful. This series was therefore abandoned in favor of a method of extending the series in Eq. (6) to give accurate values of β for large values of γ.

Derivation of Series for β

The four terms of the series in Eq. (6) fail to give values of β accurate to five places of decimals at $r/r_0=1.7$. A much improved method suggested by H. M. Mott-Smith has made it possible to determine ten more terms of this series. This method consists in expanding β, which was given as a function of γ in Eq. (5), in the form

$$\beta = A_0+A_1\gamma+A_2\gamma^2+A_3\gamma^3+ \ldots . +A_n\gamma^n+ \ldots . \tag{7}$$

[2] Due to a printer's error the coefficient of the second term was incorrectly printed $-\frac{2}{5}$ in the Phys. Rev. paper, but it was correctly given in a paper in the Phys. Zeits. J. A. Fleming pointed out this error in the Radio Review **2**, 133, 1921.

[3] Langmuir, Phys. Zeits. **15**, 351, 1914

From Maclaurin's series we have

$$\beta=\beta_0+\gamma\left(\frac{d\beta}{d\gamma}\right)_0+\frac{\gamma^2}{2!}\left(\frac{d^2\beta}{d\gamma^2}\right)_0+\cdots\cdots+\frac{\gamma^n}{n!}\left(\frac{d^n\beta}{d\gamma^n}\right)_0+\cdots \tag{8}$$

where the terms with the subscript 0 have values corresponding to $\gamma=0$. The values of the successive derivatives can be conveniently calculated as follows:

Let $\beta=a$, $d\beta/d\gamma=b$, $d^2\beta/d\gamma^2=c$, etc.

Then Eq. (5) takes the form

$$3ac+b^2+4ab+a^2-1=0 \tag{9}$$

Differentiating (9) we have

$$3ad+5bc+4b^2+4ac+2ab=0 \tag{10}$$

Differentiating (10) we have

$$3ae+8bd+4ad+12bc+5c^2+2ac+2b^2=0 \tag{11}$$

Differentiating (11) we have

$$3af+11be+4ae+18cd+16bd+2ad+12c^2+6bc=0 \tag{12}$$

From Eq. (6) we see that $\beta=0$ when $\gamma=0$. Therefore in the present expansion for β in the neighborhood of $\gamma=0$ we may place $a_0=0$ and Eq. (9) reduces to

$$b_0^2-1=0,\ b_0=1 \tag{13}$$

the positive sign being chosen since β increases with γ and hence the first derivative is positive. Substituting $a_0=0$, $b_0=1$ in Eq. (10) we have

$$c_0=-4/5 \tag{14}$$

Substituting the values of a_0, b_0, and c_0 in Eq. (11) we have

$$d_0=11/20 \tag{15}$$

Similarly from Eq. (12) we have

$$e_0=-376/1100 \tag{16}$$

By comparing (7) and (8) it is seen that

$$A_n=\frac{1}{n!}\left(\frac{d^n\beta}{d\gamma^n}\right)_0 \tag{17}$$

Therefore dividing the derived values of b_0, c_0, d_0 and e_0 by 1, 2, 6 and 24 respectively we obtain

$$A_1=1,\ A_2=-2/5,\ A_3=11/120,\ A_4=-47/3300$$

and these coefficients agree with those in Eq. (6).

It is seen that in this process when each successive equation is differentiated the new equation thus formed can be solved for a value of $(d^n\beta/d\gamma^n)_0$ by a knowledge of the values of all the preceding derivatives. Thus the coefficients of any number of terms of the series in Eq. (7) can be calculated. The 2nd column of Table I gives the first fourteen of these coefficients calculated by this method.

H. M. Mott-Smith also suggested a second series, usually more rapidly convergent than the first, which he obtained by putting

$$\beta = \theta \epsilon^{-\gamma/2}, \tag{18}$$

which reduced Eq. (5) to

$$3\theta \frac{d^2\theta}{d\gamma^2} + \left(\frac{d\theta}{d\gamma}\right)^2 - \epsilon^{\gamma} = 0. \tag{19}$$

This equation was also expanded by Maclaurin's series, using the same method as that described above.

TABLE I

Coefficients of terms in series for β

n	$\beta = \Sigma A_n \gamma^n$ A_n	$\beta = \epsilon^{-\gamma/2} \Sigma B_n \gamma^n$ B_n
0	0.0	0.0
1	+1.0	+1.0
2	−0.40	+0.10
3	+ .09166667	+ .01666667
4	− .01424242	+ .002424242
5	+ .001679275	+ .0002872294
6	− .0001612219	+ .00002658476
7	+ .00001293486	$+1.766124\times10^{-6}$
8	-8.87693×10^{-7}	$+6.332946\times10^{-8}$
9	$+5.46192\times10^{-8}$	-8.73852×10^{-10}
10	-2.94843×10^{-9}	-1.93844×10^{-11}
11	$+1.36026\times10^{-10}$	$+5.77287\times10^{-11}$
12	-7.1101×10^{-12}	$+9.4502\times10^{-12}$
13	$+2.6644\times10^{-13}$	$+4.7012\times10^{-13}$
14	$+1.2526\times10^{-15}$	-6.5539×10^{-14}

When combined with Eq. (18) it takes the form

$$\beta = \epsilon^{-\gamma/2}(B_0 + B_1\gamma + B_2\gamma^2 + \ldots + B_n\gamma^n + \ldots) \tag{20}$$

where

$$B_n = \frac{1}{n!}\left(\frac{d^n\theta}{d\gamma^n}\right)_0. \tag{21}$$

The third column of Table I gives the first fourteen coefficients and shows that this series which is at first more convergent than the A series becomes less convergent after the eleventh term.

Each coefficient of the series was checked against the corresponding coefficient of the A series by the following method. Differentiating Eq. (18) successively and placing $\gamma = 0$ and hence $\beta = 0$ and $\theta = 0$ we obtain a series of equations for $d^n\beta/d\gamma^n$ in terms of $d\theta/d\gamma$, $d^2\theta/d\gamma^2$, ... $d^n\theta/d\gamma^n$. From Eqs. (21) and (17), substituting $n!B_n = d^n\theta/d\gamma^n$ for each derivative of θ, and $n!A_n = d^n\beta/d\gamma^n$ we obtain $A_1 = B_1$; $2A_2 = 2B_2 - B_1$; $6A_3 = 6B_3 - 3B_2 + \frac{3}{4}B_1$; etc. Each coefficient was tested by means of these equations using one or two more decimal places than are given in Table I,

and all were shown to be correct within the degree of accuracy recorded in the table.

Calculation of β

Case where $r/r_0 > 1$. (Cathode inside of anode). The B series was used for all calculations of the value of β when $r/r_0 > 1$ because it is the more convergent series over the first part of the range, while over the latter part it has the advantage that the error of the neglected final terms is multiplied by the increasingly small quantity $\epsilon^{-\gamma/2}$ which becomes 0.1 at $r/r_0 = 100$. The fourteen terms were sufficient for an accurate calculation of the values of β up to $\gamma = 4.2$, $r/r_0 = 66.7$, and were useful as an approximation as far as $\gamma = 7.5$, $r/r_0 = 1808$.

In order to check the results obtained, the following method was adopted. For $\gamma = 3.0$ to $\gamma = 4.2$, β was calculated for equal intervals $\Delta\gamma = 0.2$, and in addition the value of $d\beta/d\gamma$ was calculated at each point from the equation obtained by differentiating (20). The values of β and $d\beta/d\gamma$ for each value of γ were then substituted in (5) and each equation solved for $d^2\beta/d\gamma^2$. The successive values of $d^2\beta/d\gamma^2$ thus obtained were integrated by Simpson's rule to give $d\beta/d\gamma$ and again integrated to give β, the integration in each case being checked by Weddle's rule. It was found that the values of β obtained at the end of this process as a result of integration were exactly the same as those substituted in the equation at the beginning of the process. It was therefore shown that the series calculations for β (requiring all fourteen terms at $\gamma = 4.2$) had yielded correct values which were solutions of the differential equation for β.

When the series began to fail at $\gamma = 4.2$ the integration process proved to be a practicable method of determining the correct values. For if preliminary values of β and $d\beta/d\gamma$, which are approximately correct, be substituted in the equation to obtain $d^2\beta/d\gamma^2$ and the integration process carried through as before, the result of integration will be a new set of values of $d\beta/d\gamma$ and β slightly different from the first. These new values may in turn be substituted in the equation and the process repeated, and if the final values of β do not then agree with the values obtained in the preceding approximation the process may be carried through as many times as necessary. It is found that the values of β thus successively obtained converge toward a fixed set of values which are the desired solutions of the equation, so that the method provides a means of arriving at these solutions.

From $\gamma = 4.5$ to $\gamma = 7.5$ the series calculations were used as preliminary values for the integration method, and the results of the operation of the method showed that these values of β required at $\gamma = 4.5$ a correction of

-0.00003, and at $\gamma=7.5$ a correction of -0.00260. Beyond $\gamma=7.5$ the series was abandoned and the preliminary values obtained by extrapolation.

The results of these calculations for $\gamma=3.0$ to $\gamma=10.5$ are given in Table II, together with the corresponding values of $d\beta/d\gamma$.

TABLE II

γ	β	$d\beta/d\gamma$
3.0	1.03528	+0.03506
3.2	1.04098	+ .02239
3.4	1.04440	+ .01221
3.6	1.04600	+ .00415
3.8	1.04618	− .00211
4.0	1.04526	− .00686
4.2	1.04352	− .01035
4.5	1.03986	− .01369
4.8	1.03548	− .01527
5.1	1.03084	− .01562
5.4	1.02620	− .01509
5.7	1.02182	− .01402
6.0	1.01782	− .01263
6.3	1.01426	− .01107
6.6	1.01118	− .00949
6.9	1.00856	− .00797
7.2	1.00638	− .00656
7.5	1.00461	− .00530
8.0	1.00242	− .00352
8.5	1.00101	− .00221
9.0	1.00015	− .00126
9.5	0.99970	− .00061
10.0	.99951	− .00020
10.5	.99947	+ .00001

Table III gives the complete range of values of β^2, which were all calculated to at least one more decimal place than appears in the table. The values corresponding to $r/r_0>20$ were derived from interpolations for β from Table II, using Newton's interpolation formula. They show that β^2 passes through unity at $r/r_0=11.2$, increases to a maximum value 1.0946 at $r/r_0=42$, and again passes through unity close to $r/r_0=10{,}000$. A minimum is reached just before $\gamma=10.5$ ($r/r_0=36{,}316$) and its value differs from unity by less than 0.0012. Probably from this point onward the curve passes successively through an infinite number of maxima and minima which rapidly approach unity.

It has been customary to place $\beta^2=1$ in the space charge equation (1a), but the data in Table III indicate that in the range of diameters of cathode and anode most commonly used in electron tubes (r/r_0 between 20 and 500) this practice has involved an error up to about 9.5 per cent. The reasons that this error has not been detected by experiments are probably (1) that the "end convections" are usually not accurately

known and (2) that this error is usually about equal and opposite to that introduced by neglecting the effect of initial velocities.[4]

TABLE III

β^2 as function of radius

r_0 = radius of cathode; r = radius at any point P
β^2 applies to case where P is outside cathode, $r > r_0$.
$(-\beta)^2$ applies to case where P is inside cathode, $r_0 > r$.

r/r_0 or r_0/r	β^2	$(-\beta)^2$	r/r_0 or r_0/r	β^2	$(-\beta)^2$
1.00	0.00000	0.00000	6.0	.8362	14.343
1.01	.00010	.00010	6.5	.8635	16.777
1.02	.00039	.00040	7.0	.8870	19.337
1.04	.00149	.00159	7.5	.9074	22.015
1.06	.00324	.00356	8.0	.9253	24.805
1.08	.00557	.00630	8.5	.9410	27.701
1.10	.00842	.00980	9.0	.9548	30.698
1.15	.01747	.02186	9.5	.9672	33.791
1.2	.02875	.03849	10.	.9782	36.976
1.3	.05589	.08504	12.	1.0122	50.559
1.4	.08672	.14856	14.	1.0352	65.352
1.5	.11934	.2282	16.	1.0513	81.203
1.6	.1525	.3233	18.	1.0630	97.997
1.7	.1854	.4332	20.	1.0715	115.64
1.8	.2177	.5572	30.	1.0908	214.42
1.9	.2491	.6947	40.	1.0946	327.01
2.0	.2793	.8454	50.	1.0936	450.23
2.1	.3083	1.0086	60.	1.0910	582.14
2.2	.3361	1.1840	70.	1.0878	721.43
2.3	.3626	1.3712	80.	1.0845	867.11
2.4	.3879	1.5697	90.	1.0813	1018.5
2.5	.4121	1.7792	100.	1.0782	1174.9
2.6	.4351	1.9995	120.	1.0726	1501.4
2.7	.4571	2.2301	140.	1.0677	1843.5
2.8	.4780	2.4708	160.	1.0634	2199.4
2.9	.4980	2.7214	180.	1.0596	2567.3
3.0	.5170	2.9814	200.	1.0562	2946.1
3.2	.5526	3.5293	250.	1.0494	3934.4
3.4	.5851	4.1126	300.	1.0440	4973.0
3.6	.6148	4.7298	350.	1.0397	6054.1
3.8	.6420	5.3795	400.	1.0362	7172.1
4.0	.6671	6.0601	500.	1.0307	9502.2
4.2	.6902	6.7705	600.	1.0266	
4.4	.7115	7.5096	800.	1.0209	
4.6	.7313	8.2763	1000.	1.0171	
4.8	.7496	9.0696	1500.	1.0114	
5.0	.7666	9.8887	2000.	1.0082	
5.2	.7825	10.733	5000.	1.0020	
5.4	.7973	11.601	10000.	.9999	
5.6	.8111	12.493	30000.	.9990	
5.8	.8241	13.407	∞	1.0000	∞

Case where $r/r_0 < 1$. (Cathode outside of anode). For the inverted case of electron current between concentric cylinders where the cathode is the outside cylinder, the same series may be used as in the preceding case, but γ is now negative so that alternate terms of the series have

[4] This has been discussed in a footnote to a recent paper, Langmuir, Phys. Rev. 21, 435, (1923) and illustrated by Dushman's experimental data.

changed sign. This makes the values of β negative, but since only β^2 occurs in Eq. (1) the current remains positive.

The calculations of β were made from the B series as far as $r_0/r=20$. From this point they were carried through to the end, using the A series, for after the factor $\epsilon^{\gamma/2}$ in the B series reached the value $\sqrt{20}$ it multiplied the error of neglected terms by too large a quantity. Also the A series is more convergent in this region. The results are given in Table III and are believed to be accurate to the number of places given.

For high values of r_0/r a useful approximation formula for obtaining β^2 is given by

$$\beta^2=4.6712\ (r_0/r)\ [\log_{10}(r_0/r)-0.1505]^{3/2} \tag{22}$$

This is accurate to one part in 10,000 for values of r_0/r greater than 80, and accurate within one per cent for values of r_0/r greater than 10. The equation is obtained from Eq. (19) by neglecting ϵ^γ, integrating twice, substituting the value of θ into Eq. (18) and eliminating γ by Eq. (4). The two integration constants are then so determined as to make the values of β^2 for large r_0/r agree with those calculated from the series as given in Table III.

Logarithmic differentiation of Eq. (1), considering i as constant, gives

$$3(r/V)/(dV/dr)=2+4(d\log\beta)/(d\log r) \tag{23}$$

Logarithmic differentiation of Eq. (22) gives

$$4(d\log\beta)/(d\log r)=-2-3/[\log_\epsilon(r_0/r)-0.34654]$$

Combining this with Eq. (23) we have

$$dV/dr=-(V/r)/[\log_\epsilon(r_0/r)-0.34654] \tag{24}$$

This equation for the potential gradient at any point is of course valid only in the same range as Eq. (22), that is, when r is less than say $0.1r_0$.

In the absence of electron current and the resulting space charge the field intensity between concentric cylinders is

$$dV/dr=(V/r)/\log(r_a/r) \tag{25}$$

where r_a is the radius of one cylinder at zero potential and V is the potential at any point of radius r.

Comparing Eqs. (24) and (25) we see that the field intensities become identical for all values of r if we place

$$\log(r_0/r_a)=0.34654=\log\sqrt{2}$$

or

$$r_0=r_a\sqrt{2} \tag{26}$$

The ratio $r_0:r_a$ is equal to $\sqrt{2}$ within about one part in 30,000, and therefore probably is rigorously equal to this number. This result may be interpreted as follows.

With current limited by space charge between an outer hot cathode and an inner concentric anode of small diameter, the potential distribution near the anode is unaltered if the cathode is replaced by a cold

cylinder having one half the cross section of the original cathode. The effect of space charge is thus to increase the field intensity near the anode to the same extent as a 50 per cent reduction in the cross section of the outer cylinder in the case where space charge is absent.

From this it appears that the space charge close to the anode is without appreciable effect in limiting the current.

Effect of initial velocities of the electrons. In the derivation of Eq. (2) it was assumed that the electrons leave the cathode without initial velocities. In a previous paper[5] a full discussion has been given of the effects produced by these initial velocities in the case of parallel plane electrodes.

With a cylindrical cathode of small diameter in a large coaxial anode there is a relatively high potential gradient near the cathode so that the electrons move with high velocity through the large part of their paths. The correction for the initial velocities is thus considerably less than for parallel planes (about one fourth).

In the inverted case, with the cathode as outer cylinder, the electrons move with low velocity over most of their paths. The correction for initial radial velocities must therefore be much greater than for parallel planes.

In the inverted case the tangential velocities of the emitted electrons must be of very great importance in determining the current limitation by space charge. Consider an electron which is emitted from the cathode with a tangential velocity corresponding to a fall through the potential V_0. Under the influence of the central force the electron describes an orbit in which the angular momentum is constant. The tangential velocity thus increases in proportion to the reciprocal of the radius. Since voltages are proportional to the squares of the corresponding velocities, we have

$$V_t = V_0(r_0/r)^2$$

where V_t is the voltage equivalent to the tangential velocity at a point of radius r.

If V_1 is the voltage of the anode with respect to the cathode, it is clear that $(V_t + V_0)$ cannot exceed V_1. Neglecting V_0 in comparison with V_1, we see that the only electrons which can reach the anode are those for which

$$V_0 < V_1(r/r_0)^2 \tag{27}$$

Taking the energy corresponding to the tangential velocity as $kT/2$ and placing this equal to $V_0 e$ we find

$$V_0 = kT/(2e) = T/23{,}200 \text{ (volts)}.$$

[5] Langmuir, Phys. Rev. **21**, 419, 1923

With adsorbed films of alkali metals[6] it is possible to obtain large electron currents at temperatures as low as 700°K under conditions particularly favorable for the use of a cathode outside of an anode. It is thus possible to make V_0 (for the average tangential velocity) as low as about .03 volt. With this value of V_0 and the anode voltage V_1 equal to 300, we see by Eq. (27) that $r_0/r < 100$. Thus if the diameter of the anode is less than 1/100th of that of the coaxial cathode, about half the emitted electrons cannot reach the anode because of their tangential velocities. Since these, however, contribute about equally to the space charge, the electron current flowing to the anode will be approximately half that calculated by Eq. (1). These considerations make it possible to estimate the magnitude of deviations from Eq. (1) resulting from tangential velocities and will serve as the basis for future theoretical and experimental investigations.

Lack of radial symmetry in the electrodes is another factor that can cause tangential velocity components and lead to a decrease in the space charge current.

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[6] Langmuir and Kingdon, Science, 57, 58 (1923)

THE ELECTRON EMISSION FROM THORIATED TUNGSTEN FILAMENTS

By Irving Langmuir

Abstract

Electron emission from tungsten filaments containing thoria.—Ten years ago the erratic behavior of some tungsten filaments was traced to the thoria present and it was discovered that by suitable treatment the filaments, containing 1 to 2 per cent of thoria, could be activated so as to give an electron emission many thousand times that of a pure tungsten filament at the same temperature. Extensive series of experiments have led to the conclusions summarized in this paper. The increased emission is due to a layer of Th atoms adsorbed on the surface of the tungsten. To form this layer, the thorium oxide which originally exists throughout the volume of the filament, must first be reduced in part, by heating for a few seconds to between 2600° and 2800° K; then, by heating for some time at a suitable activating temperature T_a =2000° to 2100° K, some of the Th atoms are brought to the surface by diffusing faster than they evaporate, the fraction of the surface covered θ, increasing to a limit θ_∞ which may or may not be 1. The activity determined at a lower testing temperature T_t=1400° to 1500° K, increases logarithmically with θ; for any filament it remains constant provided the filament is not heated above 1900° K and the film is not allowed to be oxidized. It is evident that the rate of activation $d\theta/dt$ depends directly on the difference between the rate of diffusion to the surface and the rate of evaporation from the surface. *Rate of diffusion of Th atoms to the surface is DG* where G is the concentration gradient (atoms per cm^4) of Th atoms near the surface, and D is the coefficient of diffusion. If N_0 is the number of Th atoms per unit area for a saturated film, it seems probable, from the crystal structures of Th and W, that N_0 is only half the number of tungsten atoms in the surface; and making correction for the increased surface due to the dodecahedral structure (6 per cent), N_0 is taken as 0.756×10^{15}. A mathematical analysis of the experimental results gives for the absolute value of D (cm^2 per sec.): $\log_{10}D = .044-20540/T$, in agreement with a theoretical expression given by Dushman and Langmuir. *Rate of normal evaporation of Th atoms* from a partly covered tungsten surface (θ=.2 to .8) in atoms per cm^2 per sec. is given by: $\log_{10}E_{nn} = 31.43-44500/T$. As the surface covered decreases below .2, E_n decreases but not as fast as θ, while for values of θ above .8, E_n increases to a value three times E_{nn}. The small variation of E_n with θ shows that the effect of adjacent Th atoms is small. Studies of the effect of prolonged activation of filaments indicate that the surface film is never more than one atom thick. Since the atoms do not diffuse back into the tungsten, we must suppose that when a Th atom diffusing to the surface arrives below another Th atom, one Th atom immediately evaporates. *The rate of induced evaporation* depends upon the diffusion and upon θ, experiments showing that $E_i = DG(0.82\theta+.18\theta^3)$. *The rate of activation* is, then, given by: $N_0 d\theta/dt = DG-E_n-E_i = DG(1-0.82\theta-.18\theta^3)-E_n$. The experimental curves, however, correspond almost equally well to the simple expression: $d\theta/dt = k(\theta_\infty-\theta)$, when θ_∞ is the limiting value, at which the diffusion and evaporation are balanced. *Deactivation*

occurs when the evaporation exceeds the diffusion. The concentration gradient G depends, of course, on the previous history of the filament, especially the preliminary reduction of thoria at a high temperature. *The rate of reduction of thoria* is given by: $\log_{10} p_r = 27.98 - 30160/T$, where p_r is the number of atoms of thorium produced per sec. per cm^3; the limiting concentration gradient (atoms per cm^4) reached is given by: $\log_{10} G_r = 25.22 - 9620/T$, the actual concentrations of thorium in parts per million by weight varying from 1.4 to 200 for temperatures of 1800° to 3000° K. Various properties of thoriated filaments in a steady state are summarized in Table VIII.

Energy changes for atoms of thorium, per gram atom, computed from constants in the above equations are: (1) *Heat of reduction of thoria in tungsten* $= -138{,}000$ cal. (absorbed); (2) *Heat of evaporation of Th from tungsten* $= 204{,}000$ cal.; (3) *Heat of diffusion of Th through tungsten*: 94,000 cal.

Crystal structure of tungsten and chromium.—Both are body-centered cubic and when etched show rhombic dodecahedron faces (110). Both show pronounced cubic cleavage (100).

EARLY in 1913 Mr. William Rogers and the writer were endeavoring to determine the electron emission from tungsten filaments in the highest possible vacuum. For this purpose two hairpin shaped filaments were mounted side by side in a tubular bulb. Two platinum wires were sealed through the glass walls on opposite sides of the bulb, the wires being bent so that the part in the bulb lay flush with the inner surface of the glass. After baking out the bulb for several hours at about 400°C and glowing the filaments, the bulb was sealed off, and one of the filaments was then heated for a considerable time at about 2900°K until enough tungsten had evaporated and deposited on the inner surface of the bulb to reduce the resistance measured between the platinum wires to about 100 ohms. Thus a gas free anode was formed and residual gases were removed by the clean-up effect of the vaporized tungsten.

The electron emissions obtained in this way were considerably larger than those previously found under less perfect vacuum conditions. Since earlier work had shown that the clean up is more effective at low bulb temperatures, the bulb was now immersed in liquid air and more tungsten vaporized. With this still better vacuum very great increases in electron emission were obtained, often of many thousand fold. The results even in this vacuum were often erratic and sometimes changed rapidly with time.

It was then found that these increases in emission depended upon the presence of small amounts of thorium in the filament. In making filaments for tungsten lamps it was customary at that time to add a fraction of one per cent of thorium oxide to prevent the occurrence of a phenomenon known as offsetting. Measurements with specially prepared pure tungsten filaments showed that the emission remained unchanged when the bulb was immersed in liquid air, and was, in fact, the same as when

the emission was measured in presence of argon at voltages high enough to ionize the gas. The lower values of the emission from the thoriated filament, obtained for example before the improvement of the vacuum, agreed fairly well with those from the pure tungsten.

During 1913 and 1914 and again especially during the last four years, very detailed studies of the mechanism of the emission from the thoriated filament have been carried out.[1] In the following pages the main conclusions reached in this work will be given, but it will only be possible to give a small fraction of the experimental evidence upon which those are based.

Conditions for obtaining high emission from a thoriated filament. If a thoriated filament is used in place of a pure tungsten filament in ordinary electron tubes, the chances are that nothing unusual will be noted in measuring electron emission, for the thorium on the surface evaporates rapidly at the normal operating temperature of a tungsten filament and is very sensitive to contamination by gases which may oxidize it. The thorium may be protected by using an exceptionally high vacuum such as that obtained by immersing the bulb in liquid air, or by vaporizing into the bulb such substances as sodium, potassium, magnesium or calcium, or traces of vapors of reducing carbon compounds such as hydrocarbons. Magnesium or calcium are most easily introduced by placing small pieces of these metals on the anode or cathode where they may be vaporized during the operation of the tube, or they may be placed on (or in) a small helical tungsten filament mounted in the bulb. Experiments have shown that the emission of a fully activated thoriated filament is the same whether the filament is in a very high vacuum or in sodium or similar vapor.

In the ordinary thoriated tungsten filament nearly all the thorium is present in the form of thorium oxide ThO_2. Apparently for this reason high emissions are ordinarily not obtained from thoriated filaments until after these have been heated to a very high temperature such as 2600°K or more. A flashing of the filament at 2800°K for 3 minutes is a sufficient preliminary treatment. This probably reduces some of the thorium oxide to metallic thorium which remains distributed at very low concentration throughout the filament. The heating to such a high temperature,

[1] The effect of thorium in increasing the electron emission from tungsten was described by the writer before the American Physical Society on October 31, 1914 (See Phys. Rev. **4**, 544, 1914) but was not published. A full description of the conditions needed to obtain this effect, together with an explanation of the phenomena, was given in U. S. Patents 1244216 and 1244217 issued to the writer on October 23, 1917. Very brief descriptions of some of the observed effects were published in Trans. Amer. Electrochem. Soc. **29**, 137, 1916; Jour. Amer. Chem. Soc. **38**, 2280, 1916, and Phys. Rev. **20**, 107, 1922.

however, removes all thorium from the surface of the filament by evaporation, so that if the temperature is lowered to say 1900°K or less and the emission is measured it is found to be the same as from a pure tungsten filament at the same temperature.

To *activate* the filament metallic thorium must be brought to the surface by diffusion from the interior. This occurs at an appreciable rate only at temperatures above about 1900°K. On the other hand at temperatures above 2200°K thorium evaporates rather rapidly from the surface of the filament. The best temperatures for activating the filament are therefore in the neighborhood of 2000°K or 2100°K.

After the filament has been brought to a very active state by this thermal treatment it will remain indefinitely in this condition if the temperature is kept below about 2100°K, provided the vacuum is sufficiently high or oxidizing gases are eliminated by the presence of easily oxidizable substances such as alkali vapors. In presence of inert gases, etc., the cathode may be deactivated by positive ion bombardment if the positive ions are given high velocities produced for example by high anode voltages.[2] With lower voltages, the thoriated filament may be kept in an active state in presence of large pressures of argon, alkali vapor, etc., even when the gas is ionized sufficiently to eliminate practically all space charge.

Measurement of the activity of the surface. The activity of the filament under various conditions is studied by measuring the electron emission (saturation current) at some fixed temperature below that at which appreciable diffusion or evaporation occurs. We shall call such a temperature the *testing temperature* and represent it by T_t. If it is desired to study states of activity ranging all the way from pure tungsten to a fully activated surface, a testing temperature of 1500°K is most convenient, for at this temperature the emission from pure tungsten is about 0.1 microampere per cm² while that from the fully activated surface is 18 milliamperes per cm², and this is a good range of current for use with a galvanometer.

The laws governing the activation of a thoriated filament are best determined by means of *activation curves* such as that illustrated by the curve *OAB* in Fig. 1. The typical experimental procedure for obtaining these data is as follows.

Three filaments *a*, *b*, and *c*, each of about 0.0075 cm diameter and 9 cm long, were bent into horseshoe shape and mounted side by side upon a single glass stem by means of platinum leads. This stem was then sealed into a tubular lead glass bulb about 13 cm long and 4.5 cm in

[2] See K. H. Kingdon and I. Langmuir, Phys. Rev. **20**, 108 (1922)

diameter provided with two flush platinum seals at opposite sides of the bulb near the centers of the filament loops. The glass stem on which the filaments were mounted had an enlargement blown in it between the seal and the flange which by casting a shadow prevented tungsten from depositing on the surface of the flange, thus avoiding leakage currents between the cathode filaments and the tungsten deposit which served as anode.

The bulb was heated several hours to 360°C while being exhausted by a glass condensation pump through a trap immersed in liquid air. During this time the filaments were heated for short times to 2000°K. After cooling the bulb to room temperature the filaments were aged for a few minutes at 2500°K. Each of the filaments was then made anode while charged to +260 volts, the other two filaments being heated to 2500°

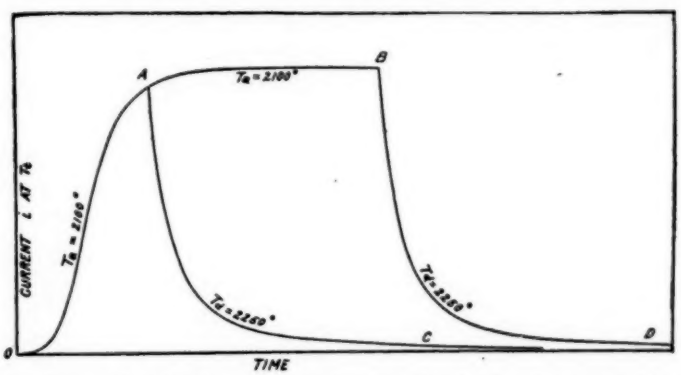

Fig. 1. Rates of activation and deactivation of a thoriated tungsten filament.

and serving as cathode. This treatment heated the platinum leads by electron bombardment. The tube was then sealed off, the bulb was immersed in cold water (or often liquid air) and the central filament (*b*) was heated at 2900° until tungsten had deposited on the walls in such amount that the resistance between the platinum flush seals was only a few hundred ohms. This tungsten deposit, connecting the two platinum seals in parallel, served as anode in all measurements of electron emission from any filament used as cathode, the unused filaments being connected to the negative end of the cathode. For these measurements the anode was kept at 250 volts, this being sufficient to give saturation with the currents used. The bulb was always kept completely immersed in liquid air when the electron emission was measured.

The filament to be studied, which usually contained from 1 to 2 per cent of thorium oxide, was flashed at 2800° for 30 seconds or more, and was then ready for obtaining data for an activation curve. After such

measurements the filament needed to be deactivated before another activation curve could be obtained. For this purpose the filament was heated for a certain time t_d to a *deactivating temperature* T_d at which thorium evaporated more rapidly from the surface than it diffused to it. Temperatures from 2200° to 2600°K were usually chosen as deactivating temperatures.

To determine the rate of activation of the filament at a given temperature the filament was first deactivated and then heated for successive periods of time at the activating temperature T_a. After each of these periods the activity of the filament was determined by measuring the electron emission at the testing temperature T_t. By plotting the electron emission i_t measured at the testing temperature T_t (say 1500°K) as ordinate, against the time t_a during which the filament has been kept at the activating temperature (2100°K) as abscissa, a curve is obtained like that shown by OAB in Fig. 1. The current at first is so small that it cannot be shown in a curve such as Fig. 1 although by using the more sensitive galvanometer shunts the currents are readily measured. After a certain time the curve rises very rapidly about like an exponential function, but then rises more slowly and finally approaches asymptotically a limiting value.

At any given point, such as A in Fig. 1, the activation of the filament may be interrupted and a deactivation curve AC may be obtained by heating the filament for successive short intervals of time at a deactivating temperature T_d which in the case illustrated was 2250°K. After each interval the filament was cooled suddenly by stopping the filament heating current so that the filament would pass rapidly through the range of activating temperatures. The temperature was then raised to the testing temperature and the emission measured.

Nature of the thorium film on activated tungsten filaments. The behavior of thoriated tungsten filaments suggests that the thorium, when it diffuses to the surface, forms an adsorbed film which completely covers the surface. The maximum activity reached by heating at different activating temperatures is the same although the rate of activation may vary greatly. It may seem strange at first that thorium can accumulate in the surface to an apparently high concentration while the concentration in the interior is very small. But this phenomenon is not different from that observed in all solutions containing a solute capable of lowering the surface energy of the solution. For example ether dissolved in water lowers the surface energy and therefore by Gibbs' rule becomes adsorbed in the surface.

The properties of thorium are such that we should expect it to lower the surface energy of tungsten. The Eötvös-Ramsay-Shields relation indicates that the surface energy of any substance at temperatures far below the critical temperature should be proportional to $T_c/V^{\frac{2}{3}}$ where T_c is the critical temperature and V is the atomic volume. Critical temperatures of substances of similar type are proportional to the boiling points at ordinary pressures. Thus for different metals the surface energies should be proportional to $T_b(d/A)^{\frac{2}{3}}$ where T_b is the boiling point, d is the density, and A is the atomic weight. Thorium seems to be about as volatile at 2000°K as tungsten is at 3000°K. The density of thorium is 11.9 while tungsten is 19.4 and the atomic weights are 232 and 184 respectively. Thus each of the three factors differs for the two metals in such a way as to make the surface energy of thorium less than that of tungsten. In fact, from the relation given above, we can calculate that the surface energy of thorium should be only 41 per cent of that of tungsten. Thorium dissolved in tungsten should therefore tend to lower the surface energy and by Gibbs' rule should be adsorbed in the surface.

During the last few years the writer has found evidence of many kinds that adsorbed films do not in general exceed a single atom or molecule in thickness.[3] The film of thorium responsible for the high electron emission from an activated filament should also not exceed an atom in thickness. The deactivation curves such as those illustrated in Fig. 1 furnish very direct confirmation of this view. The experiments show that the shape of the deactivation curve is independent of the length of time during which the filament has been allowed to activate. Thus curves AC and BD in Fig. 1 are identical although the thorium film was allowed to build up for a much longer time in one case than the other. If the film had become thicker than a single atom after the long activation at 2100° there would have been a delay in the falling off of the emission so that the slope of the upper part of BD would have been much less than that of AC.

There is another indication that the film is never more than one atom thick. If the film of thorium should continue to grow in thickness, we should not expect the increase in emission to follow any simple law, but should find a radical change in the law of increase when the film became more than one atom thick. We shall see, however, that the activation curves such as OAB in Fig. 1 are in excellent agreement with simple mathematical equations over the whole range from a fully deactivated condition to that of full activation.

[3] A full summary of this evidence with references to the original publications was given in Trans. Faraday Soc. **17**, 607 (1921) and reprinted in Gen. Elec. Rev. **25**, 445 (1922).

With this conception of an adsorbed film of thorium one atom thick, we can see that the activity of the surface should depend on the fraction of the surface covered by thorium atoms. We shall represent this fraction by θ. We now need to determine the relation between θ and the electron emission i.

It will be shown in a separate paper that the relation between i and θ may be deduced by means of the electric image theory proposed by Schottky.[5] With the accelerating fields ordinarily used in measuring saturation currents, the electron emission depends upon the number of electrons that have velocity components sufficient to enable them to reach a certain critical surface, about 5×10^{-6} cm out from the cathode surface. At the critical surface the force due to the accelerating field is equal to the attractive force (image force) acting on the electron because of the positive charge which the electron induces in the metallically conducting cathode surface. The effect of thorium in increasing the emission is not due to a specifically high emission from its surface but results from the positive contact potential of the thorium surface with respect to the tungsten surface. This positive potential of portions of the surface raises the potential at the critical surface and thus increases the number of electrons that can pass this critical region. From this theory it is found that the logarithm of the emission is a linear function of θ so that θ may be calculated from the equation

$$\theta=\frac{\log i-\log i_0}{\log i_1-\log i_0} \tag{1}$$

where i_0 is the saturation current corresponding to pure tungsten ($\theta=0$) and i_1 is that from the fully activated surface ($\theta=1$) while i is the current when the fraction of the surface covered by thorium has any value represented by θ.

If, for example, the emission from tungsten at a given temperature is one unit while that from a fully activated filament at the same temperature is 100,000 units, then the emission from a surface half covered with thorium ($\theta=0.5$) is not the arithmetic mean of 1 and 100,000 but is the geometric mean 316. Of course if the thorium on the half covered surface should be placed all at one end so that one half the length of the filament was completely covered with thorium while the other half had no thorium the emission would actually be given by the arithmetic mean 50,000. Thus the distribution of the thorium can influence the saturation current.

The electric image theory of the effect, however, indicates directly how uniform the distribution must be in order that Eq. (1) may apply.

[5] Schottky, Phys. Zeits. 15, 872 (1914)

The thorium influences the emission only by affecting the potential at the critical surface which is at a distance from the surface equivalent to about 200 atomic diameters. Any distribution of thorium which gives a nearly uniform potential at the critical surface will be sufficiently uniform to cause the emission to vary in accord with Eq. (1). Analysis shows that even if the thorium were concentrated into squares like those of a checkerboard Eq. (1) would apply fairly accurately if the squares were not larger than about 100 atoms on a side. With any distribution likely to be reached on a plane surface by diffusion or evaporation we should then expect Eq. (1) to apply.

Another relation which follows from the theoretical study of this problem is that the value of b in Richardson's or Dushman's equation for electron emission should also be a linear function of θ so that

$$\theta=(b-b_0)/(b_1-b_0) \tag{2}$$

where b_0 and b_1 correspond to the values of b for pure tungsten and for a fully activated surface, respectively.

The shape of the activation curve. Whenever the thoriated filament is heated to a high temperature at which deactivation occurs, all thorium evaporates off the surface as fast as it arrives from the interior by diffusion. In the filament just below the surface the concentration gradient should be uniform, when the concentration at the surface is zero. Thorium should thus diffuse to the surface at a practically constant rate during an activation of the filament, except in so far as the supply of thorium in the filament becomes exhausted. Since the amount of thorium needed for activation is only that in a film one atom thick, it seems probable that the available thorium in the filament should suffice for many activations. Experiments show in fact that in a series of activations alternating with deactivations at rather low temperatures where very little thorium is produced by reduction, the rates of activations decrease only very slowly in successive runs. During the early part of any single activation run we should thus expect the thorium in the surface, and therefore θ, to increase at a uniform rate. This means that the logarithm of the current should increase in proportion to the time, or the current should increase exponentially with the time. This is in general accord with the shape of the activation curve shown in Fig. 1, or curve A in Fig. 2.

Since the logarithm of the current varies linearly with θ it is more reasonable to plot an activation curve by using log i as ordinate, Curve B in Fig. 2 is plotted in this way from the same data as those used for Curve A. The current 0.01 is that from a completely deactivated surface, the dotted line MN thus corresponding to $\theta=0$. The current 1000 is from a fully activated surface, the dotted line $S'R'$ corresponding to

$\theta = 1$. Distances measured vertically between these lines MN and $S'R'$ are directly proportional to θ. Thus during the initial part of the activation run, before the current had increased to a value that can be shown on Curve A, the value of θ had risen from 0.0 to about 0.6 and the current had increased about one thousand fold. The fact that the slope of Curve B changes so little in this interval is good confirmation of the linear relation between log i and θ.

If the thorium diffuses to the surface at a uniform rate and remains in the surface, θ should increase at a constant rate and log i plotted against t_a should give a curve like MQR' instead of the observed curve B. It is clear therefore that the thorium accumulates at a decreasing rate as θ increases. It was at first thought that such an effect might be due to diffusion from the highly concentrated surface film back into the mass

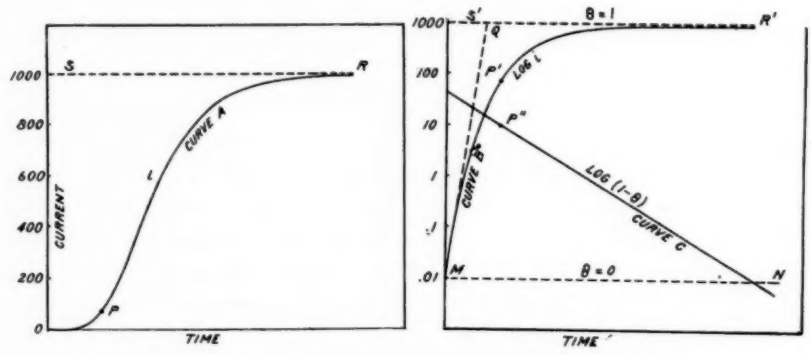

Fig. 2. Rate of activation of thoriated tungsten filaments.

of the filament. It would follow from this that the net rate of arrival of thorium at the surface should fall to zero as the surface film becomes filled ($\theta = 1$); the concentration gradient near the surface would also approach zero, while the concentration itself, just below the thorium film, would increase. The thorium which failed to accumulate in the surface would thus pile up under the surface. It is an easy matter to test whether this is so, for the increased concentration would raise the initial rate of activation in a subsequent run.

Experiments have shown that the thorium does not increase in concentration in this manner after a long activation. In a typical experiment of this kind (Exp. 528, runs M_1 to P_1) the filament was first flashed at 2800° for 23 sec. to get a high thorium content, then heated to 2500° for 100 sec. to allow irregularities in the thorium concentration to become smoothed out. The filament was now run at 2055° for 187 minutes (run M_1). The initial rate of activation (corresponding to the

straight line MQ in Fig. 2) was $d\theta/dt=0.00060$ per sec. while the final rate at the end of the run was less than 0.000003. The filament was now flashed at 2800° for less than one second to distill the thorium from the surface without producing any appreciable fresh supply of thorium. On running the filament again at 2055° (run N_1) the initial rate of activation was 0.00034 showing that the very long previous activation had not caused any accumulation of thorium under the surface but had resulted in a decrease in the thorium concentration.

The filament was kept at 2055° (still run N_1) for a total time of 277 minutes, the activation at this time having come to a standstill (rate less than 10^{-6} per sec.). In order to make sure that the flashing for 1 sec. in the previous run (which had completely deactivated the filament to $\theta=0$) had not vitiated the results by causing a loss of thorium under the surface, the filament was now only partly deactivated by flashing for 3 sec. at 2500°. This flashing lowered the value of θ to 0.78. The filament was brought again to 2055° (run O_1). The rate of activation was now $d\theta/dt=27\times10^{-6}$ per sec. whereas in the previous run (N_1) at a similar value of θ the rate had been 61×10^{-6}. If instead of continuing the runs for such great lengths of time, they were stopped after say 30 or 40 minutes, the rates of activation fell off in succeeding runs much less than in the examples shown here. In no case were any indications found of an accumulation of thorium under the surface such as would result from back diffusion from the surface film. We may therefore conclude that under ordinary experimental conditions the formation of the adsorbed film of thorium is an irreversible process in the sense that thorium never goes from the surface back into the body of the filament.

It is clear from these experiments that thorium diffuses continually to the surface of a filament even after the surface film becomes saturated. Since it does not accumulate in the film it must leave the surface in the form of vapor. This is not, however, due to ordinary evaporation of the adsorbed thorium film, for it occurs at a much lower temperature. The phenomenon we have just been discussing (falling off of $d\theta/dt$ with time) is just as well defined at an activating temperature of 1900° as at 2055° but *evaporation* of a completely formed adsorbed film takes place very slowly until temperatures of about 2150° are reached.

Examination of a large number of logarithmic activation curves (like B in Fig. 2) shows that they are accurately represented by an exponential formula of the type:

$$\log(1-\theta)=-kt \quad \text{or} \quad \theta=1-\epsilon^{-kt} \tag{3}$$

from which we obtain

$$d\theta/dt=k(1-\theta). \tag{4}$$

Let N_0 be the number of thorium atoms per cm² in a complete monatomic adsorbed film ($\theta=1$), and let G be the concentration *gradient* just under the adsorbed film, expressed in terms of atoms of thorium per cm³ per cm (atoms$\times$cm^{-4}). If D is the diffusion coefficient (in ordinary c.g.s. units, cm² sec.$^{-1}$) of thorium through tungsten at the activating temperature, then DG is the rate per unit area at which thorium atoms arrive at the surface by diffusion from the interior. If the surface has just been deactivated ($\theta=0$) no thorium leaves the surface as vapor, but that which first reaches the surface accumulates there. The rate of accumulation of thorium atoms is $N_0 d\theta/dt$ and we may therefore equate this to DG when θ is very small, that is in the range where the curve B (Fig. 2) practically coincides with the straight line MQ. From Eq. (4) we see that $d\theta/dt$ for larger values of θ is proportional to $(1-\theta)$. We may therefore place for all values of θ

$$N_0 d\theta/dt = DG(1-\theta). \tag{5}$$

By comparison with Eq. (4) we see that DG is directly related to k, the rate of activation given by the experiments:

$$DG = N_0 k. \tag{6}$$

From Eq. (5) it appears that the rate at which thorium atoms leave the adsorbed film in the form of vapor is $DG\theta$. It depends not only on the condition of the surface which is defined by θ, but upon the rate at which the thorium diffuses to the surface. We shall therefore refer to this type of vaporization as *induced evaporation* in order to distinguish it from *normal evaporation* which depends only upon the thorium present in the surface film.

The induced evaporation seems to be caused by the difference in the normal rates of evaporation of thorium atoms from tungsten and from thorium. Thus suppose that the normal rate of evaporation of separate thorium atoms in contact only with tungsten atoms is negligible at the activation temperature under consideration, but that the rate of evaporation of thorium atoms which are held by one or more *underlying thorium atoms* is very high compared to the rate of diffusion of thorium to the surface. If a thorium atom diffuses to a point on the surface already covered by thorium, it will cause the evaporation of one of the surface atoms as soon as the incoming atom reaches a position just under the surface atom. The new atom then takes the place of the atom which has just evaporated, but has not contributed anything to the thorium content of the surface. The only case in which the thorium content of the surface does increase is when a thorium atom diffuses to a point in the surface which is not already occupied by thorium. Since the chance that any given place on the surface is unoccupied is $(1-\theta)$ we are led

directly to the conclusion that the rate of growth of the thorium film is proportional to $(1-\theta)$ in agreement with the empirical Eq. (4). We have thus reached a rational derivation of Eq. (5).

If in Fig. 2 we measure distances in arbitrary units from any point P' to the dotted line $S'R'$ and plot the logarithms of these distances as ordinates of a moving point P'' we obtain the line denoted as curve C. Curves B and C are conveniently both plotted on the same sheet of semi-logarithmic paper. If the experimental observations are in accord with Eq. (3) or Eq. (5), curve C will be a straight line whose slope is equal to $2.303\ k$, if logarithms to the base 10 are used.

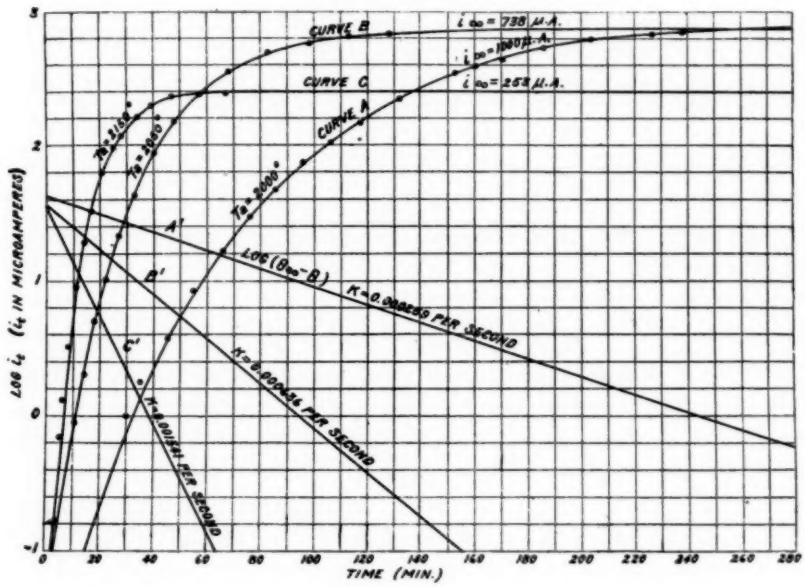

Fig. 3. Rate of activation of a thoriated tungsten filament at temperature T_a after flashing at 2800°K. (Exp. 527, V, E_1, X_1). Surface of filament = 0.217 cm²; T_t = 1445°K

Fig. 3 is an illustration of typical experimental data. The saturation currents were measured at a testing temperature of 1445°K at intervals during the activation runs. The experimentally determined points are shown by small circles on the logarithmic plots. A, B and C. Curve A is a run at an activating temperature of 2000°K. By trial it was found that the limiting value of the current towards which the observed currents were approaching asymptotically was 1000 microamperes. A horizontal line was drawn corresponding to this current and distances were measured vertically in cm from this line to the observed points on Curve A. These were plotted logarithmically (by the method described for curve C,

Fig. 2) and gave the straight line A'. From this straight line by reversing the above process, the curve shown by the full line marked curve A was calculated. It will thus be noted that curves A, B, and C in Fig. 3 are not merely smooth curves drawn to fit the observations but they are true exponential curves calculated from equations like Eq. (3) by the choice of suitable values of k. It is seen from Fig. 3 that the observed points fall on the calculated curve with high accuracy except for very low values, in the neighborhood of $\log i_l = 0$, which corresponds to currents of about one microampere. Since the currents in this particular set of experiments were measured with a portable microammeter the agreement is still within the error of measurement.

Other experiments made at higher testing temperatures or with more sensitive instruments have shown that the agreement with the exponential equation is, in general, equally good down to the lowest states of activity (where $\theta = 0$). These results not only confirm Eq. (5), but check the accuracy of Eq. (1) and indicate that the whole activation curve follows a single simple law. It is this evidence that was referred to previously in connection with the proof that the thorium film is monatomic.

Evaporation of thorium and deactivation curves. Although the rates of activation could be made to vary widely, even at a given activating temperature, by changing the concentration gradient G, practically the same limiting value of $i_\infty = 1000$, at $T_l = 1445°\text{K}$, was found repeatedly in separate runs at activating temperatures ranging from 1900° to 2100°. But if G had an unusually low value, as for example after heating the filament for many hours at 2300°, the limiting currents found with activating temperatures of 2000° or more were distinctly lower. This effect is due to normal evaporation of thorium from the surface at a rate comparable with the rate of supply of thorium by diffusion from the interior.

Curve C in Fig. 3 at an activation temperature of 2150° illustrates the effect of this evaporation. The rate of activation is much greater than in A, for the rate of diffusion is increased by the higher temperature. But the limiting current i_∞ has fallen to 253 microamp., which corresponds to $\theta_\infty = 0.88$.

If we are to take into account normal evaporation of thorium, Eq. (5) must be modified by subtracting from the second member a term E which we may define as the rate of evaporation expressed in atoms per second per cm^2 of filament surface. The quantity E will depend on the temperature and on θ. The most natural supposition, perhaps, is to assume that E is proportional to θ, viz., the evaporation is proportional

to the amount of thorium on the surface. But we shall see that the experiments indicate that this is not the case. When the surface is very largely covered with thorium it is in fact to be expected that the thorium atoms will tend to hold on to each other and so make the rate of evaporation increase less rapidly than in proportion to θ. Since it is convenient to have an expression for the variation of E with θ let us assume provisionally that E is a linear function of θ. This will always be permissible within a restricted range of values of θ. We may thus place

$$E=\nu_0+\nu\theta. \tag{7}$$

Subtracting this from the second member of Eq. (5) gives

$$N_0 d\theta/dt=DG(1-\theta)-(\nu_0+\nu\theta). \tag{8}$$

When $t=\infty$, $d\theta/dt=0$ and $\theta=\theta_\infty$, so the equation becomes

$$\nu_0+\nu\theta_\infty=DG(1-\theta_\infty). \tag{9}$$

Subtracting (9) from (8) and integrating

$$\log\left(\frac{\theta_\infty-\theta}{\theta_\infty-\theta_0}\right)=-kt \tag{10}$$

where θ_0 is the value of θ corresponding to $t=0$ and k is a constant

$$k=(DG+\nu)/N_0. \tag{11}$$

The limiting value of θ is θ_∞ given by

$$\theta_\infty=(DG-\nu_0)/(DG+\nu). \tag{12}$$

The experimental data furnish us with values of k and θ_∞ and from these we wish to find DG, ν_0 and ν. From the above equations we find

$$DG=N_0k-\nu=N_0k\theta_\infty+\nu_0 \tag{13}$$

$$\nu_0+\nu=N_0k(1-\theta_\infty). \tag{14}$$

When $\theta_0=0$ and $\theta_\infty=1$, Eq. (10) reduces to Eq. (3). When the rate of evaporation ν is not negligible compared to the rate (DG) at which thorium diffuses to the surface, we see from Eq. (12) that θ_∞ is less than unity, so that the filament does not become fully activated. The linear relation between $\log(1-\theta)$ and t given by Eq. (3), which agreed with experiments where no evaporation occurred, must now be replaced according to Eq. (10) by a linear relation between $\log(\theta_\infty-\theta)$ and t.

Thus in Fig. 3 the lines B' and C' were obtained by plotting as ordinates the logarithms of the vertical distances from points on the curves B or C to the horizontal asymptotes corresponding to the values of i_∞ for the curve in question. It is seen that the agreement between the observed points on curves B and C is as good as it was in the case of curve A. It should be kept in mind that the curves A, B and C were *calculated* by means of Eq. (10), choosing of course in each case values of θ_∞ (or i_∞) and k which gave best agreement with the experiments. Activation curves taken under the most varied conditions, even at such high

activating temperatures that θ_∞ did not exceed 0.1, always gave reasonably good agreement with straight lines when plotted in the manner of curves A', B' and C'.

Run X_1 in Fig. 4, is an example of a *deactivation curve* obtained with the filament at a deactivating temperature T_d of 2300°. Preceding this run the filament had been flashed 30 seconds at 2800°, then run 3 hours

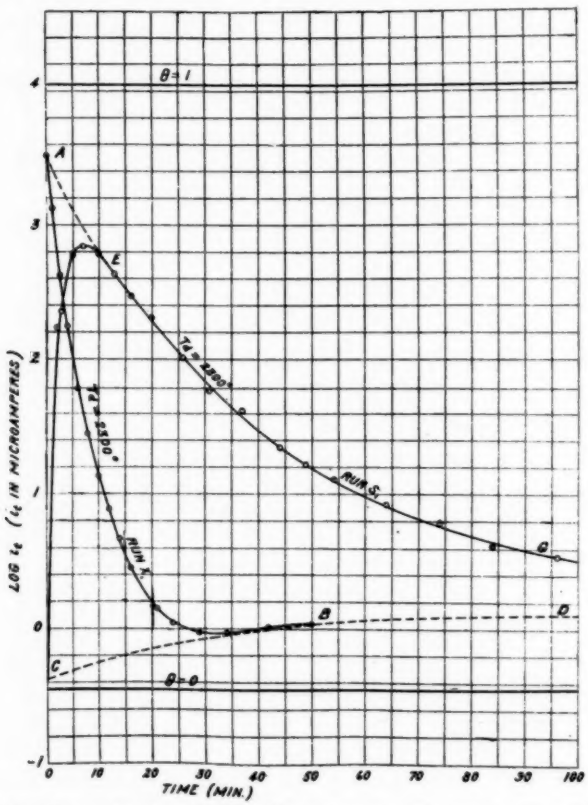

Fig. 4. Deactivation of a thoriated tungsten filament at $T_d = 2300°$K. $T_t = 1630°$K.

at 2250° and 3 hours at 2100°. This had caused about 4/5 of the thorium produced at the high temperature to diffuse out of the filament and had thus lowered G to about 1/5 of its value after flashing. In run X_1, the activity falls rapidly at first, reaches a minimum and slowly rises to a steady value. This is characteristic of all deactivation curves in which G has previously been brought to a low value.

The reason for the minimum is that the activity depends upon two factors that act in opposite directions; the activity tends to decrease

because of evaporation but the increased production of thorium in the filament due to the higher temperature increases G and tends to raise the activity. Since the latter effect occurs more slowly than the former it is readily seen that the activity should have a minimum.

A second type of deactivation curve, illustrated by run S_1, Fig. 4, is obtained if the filament is flashed at a high temperature so as to give a high value of G and is then immediately run at a lower temperature. In the case of run S_1 the filament was flashed for 30 seconds at 2800° and then run at 2300° for 106 minutes, the activity being measured at intervals at a testing temperature of 1630°. In this case the activity rises rapidly to a maximum and then falls slowly to the same limiting value (D in Fig. 4) as in the first type of activation curve. There is no minimum activity in this case. The reasons for this shape of curve are similar to those of the first type, but the displacements from the stationary state are in opposite directions. At the beginning of the run there is no thorium on the surface so that evaporation cannot occur, but the thorium arrives at the surface at a rapid rate because of the high value of G. The activity thus increases. In the meantime, however, the thorium is diffusing out of the filament faster than it is being produced so that the value of G steadily but slowly decreases causing finally a decrease in the activity.

In the latter part of both types of curve of Fig. 4 the thorium evaporates from the surface at nearly the same rate as it arrives from the interior so that in a sense a "steady" state may be said to have been reached although this state gradually changes as G increases or decreases. In the first parts of the curves, however, the rates of evaporation and diffusion are not even approximately balanced, the conditions approaching those assumed in the derivation of Eqs. (10) and (11). The steady state corresponds to the case where $\theta=\theta_\infty$ as given by Eq. (12). The dotted curve AE in Fig. 4 is drawn as a continuation of EG and the whole curve AEG corresponds to values of θ_∞. The sharply rising initial part of run S_1, marked CE, is thus an activation curve like those illustrated in Fig. 3 except that the value to which the curve approaches (corresponding to θ_∞) is not constant but decreases according to curve AEG. Similarly, CBD represents the limiting current values corresponding to θ_∞ for run X_1.

From the curves of Fig. 4 we see that the times required for the activity to go 90 per cent of the way to the "steady" value was 4.5 minutes for run S_1 and 19 minutes for run X_1, these being in a ratio of 1 : 4.2. From Eq. (11) this must also have been the ratio of the corresponding values of $(DG+\nu)$ so that DG in run X_1 must have been at least 4.2 times as great as in run S_1.

We shall return to a quantitative consideration of activation and deactivation curves after the following section.

Arrangement of tungsten and thorium atoms in surface films. Tungsten crystallizes with a body-centered cubic lattice of atoms, the side of each cube being 3.150 A.[6] The shortest distance between atoms (from the center atom to an atom in a corner) is $\sqrt{(\frac{3}{4})} \times 3.150$ or 2.728 A. In a plane (100) through any atom parallel to a face of the elementary cube the number of atoms per cm² is 1.008×10^{15}. In a plane passing through the center atom and any of the edges of the cube (i. e. 110 plane) there are 1.425×10^{15} atoms per cm².

By special heat treatment a square tungsten rod (8×8×100mm) was brought into the form of a single crystal. As it had been held for a long time near its melting point, the surface was distinctly etched by evaporation so that it reflected light in several directions which were not related to the original faces of the rod. By mounting a fragment of this rod on a cork and holding the specimen in a dark room so that the etched crystal faces reflected light from a single lamp placed almost behind the observer's head, it was possible to place pins in the cork indicating the directions of the normals to the crystal faces. Inspection of these pins proved that the faces developed by etching are those of the rhombic dodecahedron (110 planes), all these 12 faces and no others being observed. These are the faces which contain the greatest possible number of atoms. Other single crystals of tungsten were chemically etched by an alkaline ferricyanide solution but only the same faces were found.[7] Tungsten surfaces which have been heated to such high temperature that some evaporation has occurred, thus consist exclusively of dodecahedral faces. Simple considerations show that the extent of the total developed surface does not increase as the size of the faces increases.

Consider, for example, a single crystal of tungsten having the external form of a sphere, and let this be etched until the original surface is gone and has been replaced by etched dodecahedral faces. Imagine that the sphere be viewed from a point far out along one of the cubic

[6] Hull, Phys. Rev. **17**, 576 (1921)

[7] The cleavage surfaces of the single crystal rod were found to be cubic faces (100 planes). Chromium which belongs to the same group in the periodic table, and crystallizes with the body centered cubic lattice, showed pronounced cubic cleavage (100 planes) with a less well developed secondary cleavage along the dodecahedral faces (110 planes). After placing a fragment in dilute hydrochloric acid for a few hours the cubic faces disappeared and the dodecahedral faces were all brought out distinctly. Large crystals of iron, (transformer iron containing a few per cent of silicon) which also showed the body centered lattice, gave on etching in acid only the cubic faces (100 planes).

axes, say the X-axis. From this position only faces parallel to four out of the 12 dodecahedral faces can be seen and each of these faces is inclined at 45° to the line of sight. Every part of the crystal that can be seen must consist of just such faces. Thus if r is the radius of the sphere, the apparent or projected area is πr^2 but the actual area seen is $\sqrt{2}\cdot\pi r^2$.

As this represents only 4 of the 12 faces, the total surface of the etched sphere is $3\sqrt{2}\cdot\pi r^2$ as compared with $4\pi r^2$ for the original sphere. The effect of etching has thus been to increase the surface $3/(2\sqrt{2})=1.0607$ fold. The depth of etching has no influence on this ratio as long as the *projected* area of the sphere is not materially changed. The *total surface* of a tungsten filament consisting of small crystals oriented at random *is thus 6 per cent greater than its apparent surface.*

Thorium crystallizes in a face-centered cubic lattice[8], the side of the cube being 5.04 A. Since this is a close-packed type of lattice, the thorium atoms behave much like spheres of diameter 3.564 A. The number of such spheres that can be packed per cm² into a plane lattice is 0.909×10^{15} which is only 64 per cent as many as the atoms in the 110 planes in tungsten. We shall see from the data on evaporation of thorium, that forces between adsorbed thorium atoms and the underlying tungsten atoms are very large while those between thorium atoms in adjacent positions on the surface are relatively small. It is therefore highly probable that there is a stoichiometric relation between the number of thorium atoms in a fully active surface and the number of underlying tungsten atoms. A one-to-one relation would involve excessive crowding of the thorium atoms and would be incompatible with small forces between adjacent atoms. We shall therefore assume that there are half as many thorium atoms as underlying tungsten atoms in a fully active surface. Thus the maximum number of thorium atoms in a plane surface is 0.7136×10^{15} per cm². In the case of the surface of an ordinary tungsten filament we must apply the correction due to etching (1.0607) so that the quantity that we have called N_0 in Eqs. (5) to (14) should have the value

$$N_0=0.756\times10^{15} \text{ atoms per cm}^2. \tag{15}$$

Rate of activation as a function of temperature. At temperatures so low that evaporation of thorium is negligible, the rate of activation, as measured by k, is proportional to the product DG according to Eq. (6). By proper preliminary heat treatment G can be brought to the same value in each of a series of runs carried out at different temperatures. The rate of activation k is then a relative measure of the diffusion coefficient D.

[8] Hull, Phys. Rev. **18**, 88 (1921)

Table I gives the results of such a series of runs (in the latter part of Exp. 527). Immediately preceding each run the filament was flashed at 2800°K for 5 seconds to bring G to a definite and constant value. The filament temperature was then changed to T_a (Col. 2), this being interrupted at intervals ranging from 5 to 20 minutes for the purpose of measuring the activity at the testing temperature (T_t) of 1445°K. The saturation currents at T_t were plotted on semi-logarithmic paper as illustrated in Fig. 3. The limiting current i_∞ corresponding to $t=\infty$ is given in microamperes in Col. 3. The filament surface from which these currents were obtained was 0.217 cm². By plotting $\log_{10} i_\infty - \log_{10} i$ as ordinate (on the same sheet of semi-logarithmic paper), against time as abscissa, straight lines were obtained as in curves A', B', and C' in Fig. 3. The slopes of these lines, after multiplying by 2.303 to convert to natural logarithms and dividing by 60 to convert from rates per minute to rates per second, give directly the values of k defined by Eq. (10). These are tabulated in Col. 4. Col. 5 gives θ_∞ calculated by Eq. (1) from i_∞ of Col. 3 using the values $i_1=1300$ and $i_0=0.013$ microamperes. Col. 6 gives values of θ_∞ calculated by means of Eq. (14) from data on ν_0 and ν and will be discussed in a later section.

TABLE I

Rates of activation at various temperatures

Experiment 527 Filament surface 0.217 cm²

(1) Run	(2) T_a	(3) i_∞ μ-amps. at $T_t=1445$°K	(4) k (10^{-4} per sec.)	(5) θ_∞ (obs.)	(6) θ_∞ (calc.)
X	2050°K	790	5.31	0.957	0.958
Y	2050	738	6.36	0.951	0.964
Z	2150	253	15.41	0.856	0.856
A_1	2105	477	9.29	0.913	0.913
B_1	2050	707	5.11	0.948	0.957
C_1	2050	805	5.15	0.958	0.957
D_1	1950	1300	1.70	1.000	0.990
E_1	2000	1000	2.59	0.977	0.976

The diffusion of one metal through another must involve interchanges in position between neighboring atoms in the space-lattice. Only atoms containing a certain critical amount of kinetic (or potential?) energy are capable of making such interchanges. The frequency of these changes of position and therefore the diffusion coefficient should thus be proportional to $\epsilon^{-Q_D/RT}$, where Q_D may be taken as the "heat of diffusion" or the critical energy (per gram atom) involved in atomic interchanges.[9] From this relation it appears that the natural logarithm of the diffusion

[9] S. Dushman and I. Langmuir, Phys. Rev. **20**, 113 (1922)

coefficient is a linear function of the reciprocal of the temperature, the slope of this line being equal to Q_D/R.

To test this conclusion the values of $\log_{10}k$ from Table I have been plotted, in Fig. 5, against $1/T_a$. Since 4 runs were made at $T_a=2050°$, the average was taken of the values of k for these runs, viz. $k=0.000548$. The points lie close to a straight line. Taking $R=1.987$ calories this slope gives $Q_D=94000$ calories per gram atom.

Absolute value of the diffusion coefficient. To determine the actual value of the diffusion coefficient we need to measure some property involving the total thorium content of the filament. Heating the filament momentarily to a very high temperature increases the concentration of

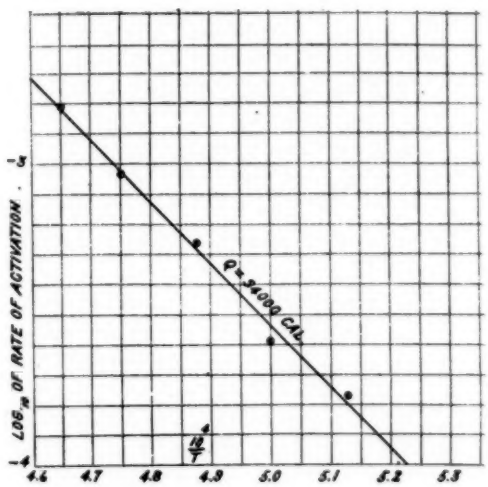

Fig. 5. Rate of activation of thoriated filaments as function of temperature.

thorium. By heating the filament for a long time at a much lower temperature this supply of thorium gradually diffuses out so that the concentration gradient at the surface decreases in proportion. By measuring the product DG from time to time during this exhaustion of the thorium supply, it is possible to determine the absolute value of D.

The diffusion problem involved is analogous to the thermal problem of the cooling of a long cylinder suddenly plunged into a perfectly conducting fluid maintained at a fixed temperature.

This problem has been treated by Carslaw[10] who gives the general equations for the temperature distribution in an infinite cylinder resulting from any initial distribution. For the particular cases required in the

[10] Carslaw, Fourier's Series and Integrals, Macmillan and Co., 1906, p. 316

present problem Mr. Harold Mott-Smith has derived the following equations.

Consider an infinitely long circular cylinder in which the concentration (of thorium) is a function $f(r)$ involving only the distance r from the axis of the cylinder. At a certain instant, which we shall choose as origin of time, $(t=0)$, the concentration over the whole surface of the cylinder is brought to zero and kept at zero. This is actually accomplished by raising the temperature of the filament suddenly at the time 0 to such temperature that all the substance that diffuses to the surface evaporates immediately. Then after the time t, the *concentration gradient* G at the outer surface of the cylinder is expressible as an infinite series of exponential terms:

$$G=\Sigma B_n\epsilon^{-P_n} \tag{16}$$

where

$$P_n=\mu_n^2Dt/R^2 \tag{17}$$

Here R is the radius of the cylinder and D is the diffusion coefficient. The quantities μ_n are the successive roots of the equation $J_0(x)=0$, where $J_0(x)$ is the zeroth order Bessel function of x. In using the foregoing equations it is merely necessary to substitute the following numerical values of these constants:[11]

$$\mu_1^2=5.783 \qquad \mu_3^2=74.89$$
$$\mu_2^2=30.47 \qquad \mu_4^2=139.04 \tag{18}$$

The coefficients B depend upon the initial distribution of the diffusing substance, at the time $t=0$. In case the *concentration* is initially uniform throughout the cylinder and equal to C_u we find

$$B_1=B_2=B_3=\ \ldots\ =2C_u/R \tag{19}$$

If the diffusing substance is being produced at a uniform rate throughout the whole body of the cylinder while the concentration at the surface is kept zero, the concentration finally assumes a parabolic distribution given by

$$C=C_\phi[1-(r/R)^2] \tag{20}$$

where C_ϕ is the concentration at the axis of the cylinder and C is the concentration at any point whose distance from the axis is r. The concentration gradient G at the surface is then

$$G=2C_\phi/R \tag{21}$$

If the production of diffusing substance is suddenly stopped after this parabolic distribution has been reached, as for example by lowering the temperature, the subsequent changes in G are still given by Eq. (16) but the values of the coefficients B now become

$$B_n=8C_\phi/(\mu_n^2R) \tag{22}$$

[11] Smithsonian Physical Tables, 1920, p. 68

From Eq. (19) the initial value of G is infinite for the case of initial uniform distribution. With the parabolic distribution, we see from Eqs. (16) and (22) that the initial value of G is $8C_p[\Sigma(1/\mu_n^2)]/R$ which is the same as given by Eq. (21).

From the rapid increase in the exponents (18) in the series (16) it is evident that no matter what the initial distribution may be, the higher terms of the series soon become negligible compared to the first term. Curve II in Fig. 6 is a logarithmic plot of G as a function of time for the

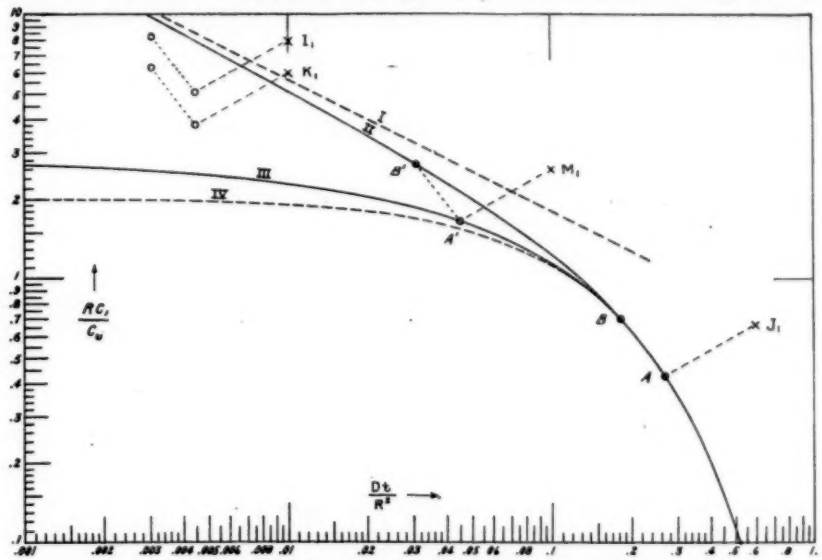

Fig. 6. Transient effects in diffusion in filaments

Curve I. Initial uniform distribution in semi-infinite solid with plane face.
Curve II. Initial uniform distribution in cylinder.
Curve III. Initial parabolic distribution in cylinder.
Curve IV. First term in series, Eq. (23).

case of initially uniform distribution corresponding to Eqs. (19) and (16). As ordinate, RG/C_u is plotted on the logarithmic scale, while Dt/R^2 is the abscissa on the same scale. This method of plotting has the advantage that any factorial change in R or D or the units in which these or t are expressed, does not change the shape or scale of the curve, but is equivalent to a displacement of the origin of co-ordinates. Curve IV corresponds to the *first term* of the series (16) with the value of B_1 from Eq. (19):

$$G=(2C_u/R)\epsilon^{-\alpha t} \tag{23}$$

where by Eqs. (17) and (18)

$$\alpha=5.783D/R^2 \tag{24}$$

It is seen from Fig. 6 that even when the initial concentration is uniform, G is given with high accuracy by Eq. (23) for all values of t

which make Dt/R^2 greater than about .16. Let us consider on the other hand the case where the diffusion has proceeded for only a short time so that the concentration in the cylinder differs appreciably from the original uniform concentration only in layers whose depth below the surface is small compared to the radius. Then the conditions are essentially similar to those occurring when the plane surface of a semi-infinite solid is suddenly changed in temperature, a problem treated in most books dealing with heat conduction.[12] Thus for the corresponding diffusion problem, when the initial concentration is uniform and the concentration at the surface is brought to zero, we find

$$G = C_u/\sqrt{\pi Dt} \tag{25}$$

To compare this with the functions plotted in Fig. 6 it is conveniently transformed into

$$RG/C_u = 0.564\sqrt{R^2/(Dt)} \tag{26}$$

which corresponds to the straight line I. For very small values of Dt/R^2 Curve II approaches I but rather slowly.

If the initial distribution is of the parabolic type given by Eq. (20), the concentration gradient G is also expressible, for sufficiently large Dt/R^2, by the first term of Eq. (16) which now by Eqs. (17), (18), (22) and (24) takes the form

$$G = 1.3833(C_p/R)\epsilon^{-\alpha t}. \tag{27}$$

By comparing this with Eq. (23) we see that both these functions can be expressed by Curve IV in Fig. 6 if we take

$$C_p = 1.4458C_u. \tag{28}$$

In other words the distribution finally becomes the same whether we have initially a uniform concentration or a parabolic distribution with the concentration at the axis 1.446 times as great. Curve III in Fig. 6 gives the values of RG/C_u for this case calculated by means of the *complete* series of Eq. (16) using the coefficients given by Eq. (22). Eq. (27) thus gives a good approximation whenever Dt/R^2 exceeds 0.1.

The total amount q of diffusing substance in the cylinder per unit of length is $\pi R^2 C_u$ when the concentration is uniform. For the parabolic distribution we find from Eq. (20) by integration

$$q_p = \tfrac{1}{2}\pi R^2 C_p. \tag{29}$$

When the distribution has become such that G falls off in accord with Eq. (23) or with Curve IV in Fig. 6, we may find q at any time t from the value of G in Eq. (23) by calculating the total amount of substance that diffuses out to the surface of the cylinder between $t = t$ and $t = \infty$. This gives:

$$q = (4\pi R^2 C_u/\mu_1^2)\epsilon^{-\alpha t} = 2.1729R^2 C_u \epsilon^{-\alpha t} \tag{30}$$

[12] See for example Ingersoll and Zobel, Theory of Heat Conduction, p. 77

The distribution within the cylinder under these conditions (i. e., when G is expressible as the first term of the series of Eq. 16) is given by

$$C = 0.8018 RG J_0(\mu_1 r/R) \tag{31}$$

where C is the concentration at any point whose distance from the axis is r. The concentration at the axis is thus equal to $0.8018\ RG$.

The absolute value of the diffusion coefficient is most easily found from experiments carried out under conditions such that G varies with time in accord with Eqs. (23) or (27). The experiments on rates of activation of the filament in successive stages thus furnish data for the evaluation of a and from this by Eq. (24) the value of D is calculated.

Several sets of experiments were made to determine D at various temperatures. Most of these were carried out before the complete theory of the diffusion had been worked out, so that the experimental conditions have not always been chosen as well as would otherwise have been possible.

Table II contains data for the calculation of the diffusion coefficient at 2500°K, obtained from Exp. 528. Preceding each of these runs I_1 to M_1 the filament was flashed at 2800°K for 23 seconds in order to bring the thorium content to a definite value. The filament was then maintained at 2500°K for the time given in Col. 2 with the object of causing the concentration gradient G to decrease according to Eq. (16). After the heating at 2500°, the rate of activation k(Col. 4) was measured by running the filament at $T_a = 2055$°K, interrupting this run at frequent intervals for testing the activity at $T_l = 1450$°K in the usual way.

TABLE II

Rates of activation at 2055°K following deactivation at 2500°K for various times

Experiment 528 Filament surface 0.217 cm²

(1) Run	(2) Time at 2500°K (sec.)	(3) i_∞ at 1450°K (μ-amp.)	(4) k at 2055° (per sec.)	(5) θ_∞ from i_∞ (obs.)	(6) θ_∞ (Eq. 42) (calc.)	(7) $k - k_r$ ($\times 10^{-4}$)
I_1	10	760	11.49×10^{-4}	0.976	0.981	7.85
J_1	600	548	4.31	0.947	0.949	0.67
K_1	10	780	9.58	0.978	0.977	5.94
L_1	3660	505	3.64	0.941	0.940	0.00
M_1	100	720	6.22	0.970	0.965	2.58

The values of θ_∞ in Col. 5 were calculated by Eq. (1) from i_∞ in Col. 3 taking $i_0 = 0.01$ and $i_1 = 1000$ microamp. The calculated θ_∞ in Col. 6 will be discussed later.

Examination of the data in Col. 4 shows that k decreases rapidly at first and then approaches a limiting value of 3.64×10^{-4} which we shall represent by k_r. In this *stationary state* thorium is being reduced from the

oxide at the same rate as it is lost by diffusion and evaporation. The values of k are proportional to G, so that the equations that we have derived for the variations of G should be directly applicable to our experimental data. Because of the constant production of thorium, however, we use for this purpose not k but $k-k_r$ as given in Col. 7 of Table II. Thus after sufficient time has elapsed for the effect of the higher terms in Eq. (16) to die out, the decay of the quantity $k-k_r$ should follow the exponential law given by Eq. (23). The following method allows us to compare the experimental data directly with the complete Eq. (16) as represented by the curves in Fig. 6.

It is evident that a plot of $\log(k-k_r)$ as a function of $\log t$ should have the same shape and scale as the corresponding curve in Fig. 6 and should differ only by a parallel displacement. The points marked I_1, K_1, M_1, and J_1 are placed in Fig. 6 by plotting $10^4(k-k_r)$ from Col. 7 of Table II against $10^{-3}\cdot t$ where t is the time in seconds from Col. 2. By transferring these points to tracing paper and sliding the paper so as to keep its lower edge horizontal, it is possible to bring any two of the points such as J_1 and M_1 to lie on any desired curve. For example by displacing the tracing paper parallel to the line J_1A the points J_1 and M_1 are brought on to the curve III, which corresponds to the case of parabolic distribution. The points I_1 and K_1, however, do not fall on this curve but lie between II and III. By displacing the tracing paper by the distance AB the points J_1 and M_1 are brought on to the curve II, corresponding to uniform initial distribution. The points I_1 and K_1 then lie too low. It appears from this that the distribution of thorium is intermediate between the two cases considered. It is more likely, however, that the true distribution resulting from the production of thorium by heating the filament to high temperature approaches closely to the parabolic case if sufficient time is allowed for a stationary state to be reached. It is rather doubtful if the 23 seconds allowed in these experiments was long enough. Failure to reach the stationary state would cause deviations of the type observed.

By having placed the observed points on the theoretical curve in this manner, we determine the absolute value of Dt/R^2, and from this since t and R are known, we find D. Thus if we assume initial parabolic distribution we find Dt/R^2 for the point A to be 0.27. For this point $t=600$ sec., and therefore since $R=0.00389$ cm we find $D=6.8\times10^{-9}$ cm^2 per second for 2500°K. Similarly if we assume initially uniform distribution, Dt/R^2 for point B is found to be 0.18 which gives $D=4.3\times10^{-9}$ cm^2/sec. Of course the same values for D are found from the other pairs of points.

The diffusion coefficient at 2055°K was determined by a series of prolonged activation runs, N_1, O_1, and P_1 carried out at this temperature. Just preceding run N_1 the filament was flashed for a couple of seconds at 2800°K. In run N_1 the filament was maintained at 2055° for 277 minutes, the activity being tested at frequent intervals in the usual way. The filament was then flashed at 2500° for 3 seconds, a time so short that the filament was only partly deactivated and G was not altered. Run O_1 then followed, the filament being kept at 2055° for 110 minutes. After flashing for 4 seconds at 2500° an activation curve was again made (run P_1) at 2055°. Selecting from these runs points corresponding to a definite value of θ we obtain the following data[13]

Run	t	k	$k-k_r$
N_1	30 min.	3.59×10^{-4}	3.06×10^{-4}
O_1	305	1.62	1.09
P_1	475	1.25	0.72

Plotting these on tracing paper and comparing with the Curve III of Fig. 6 the most probable value of the diffusion coefficient at 2055° is found to be 1.1×10^{-10} cm^2 sec.$^{-1}$.

The deactivation curve of run S_1 shown in Fig. 4 furnishes excellent data for the calculation of D at 2300°. We have seen that the portion EG of the curve CEG results from the gradual decrease in G as the supply of thorium becomes exhausted. In the region represented by CE the rate of change of activity is so great that the term $N_0 d\theta/dt$ in Eq. (8) is at least comparable in magnitude with the terms in the second member of the equation. In the region EG, however, $d\theta/dt$ has become so small that the corresponding term may be neglected in comparison with those in the second member. Eq. (8) thus becomes

$$DG=(\nu_0+\nu\theta)/(1-\theta) \tag{32}$$

The quantity G given by this equation cannot be used directly to determine the diffusion coefficient according to Eq. (16), for the constant production of thorium at 2300° must be allowed for. Let G_r be the limiting value of G which would be reached when the accumulated surplus of thorium has been exhausted, the rate of loss of thorium by diffusion being then equal to the rate of production. The value of G_r can be expressed in terms of θ_r, the corresponding value of θ, by an equation similar to Eq. (32). We now substitute in the diffusion equations the quantity $(G-G_r)$ just as we previously used $(k-k_r)$. Eq. (32) gives

$$\frac{D}{\nu+\nu_0}(G-G_r)=\frac{1}{1-\theta}-\frac{1}{1-\theta_r} \tag{33}$$

[13] The value of k_r was taken to be 0.53×10^{-4} as calculated from values of G_r which will be discussed later.

The quantities in the second member are both easily found from the experiments. Taking the logarithm of the second member and plotting against the logarithm of the time as in Fig. 6, the absolute value of D is found. The data of run S_1 in Fig. 4, are in complete agreement with the curves of Fig. 6, in the range beyond $t=40$ minutes corresponding to the region where the curves II, III and IV coincide. For smaller values of t, the experimental curve lies somewhat above Curve II. This should not be taken as evidence, however, that there is a uniform rather than a parabolic distribution of thorium in the filament for it is probable that the deviations from the Curve III are due to variations of the rate of evaporation as a function of θ, from the linear relation assumed in Eq. (7) upon which Eq. (33) is based. The assumption of this linear relation is always justifiable over a narrow range of values of θ, but becomes open to question when applied to the wide range covered by the data of run S_1.

If we therefore confine our attention to the portion of run S_1 taken after the first 40 minutes we find by our comparison with Fig. 6 the value $D=1.12\times10^{-9}$ cm^2 sec^{-1}. Since in this region the effects of the uncertain initial distribution of thorium are eliminated, so that only the first term in the series of Eq. (16) need be considered, a simpler method may be employed. Plotting the $\log_{10}$ of the second member of Eq. (33) against the time t (on semi-logarithmic paper), a straight line is obtained. The slope of this line, multipled by 2.303, gives directly the value of α defined by Eq. (24). From this the value of D is found, and is of course the same as that obtained by the curves of Fig. 6.

Run T_1 was made to determine the diffusion coefficient at 2400°. The filament was first flashed at 2800° for 30 seconds and then run at 2400° for deactivation, the activity being measured at a testing temperature of 1800°. The run was interrupted three times for the purpose of determining the value DG/N_0 by means of very short activation runs of 5 to 10 minutes at 2100°. The values of θ and $d\theta/dt$ were found in these runs from which, by Eq. (8), DG/N_0 could be calculated, the term $(\nu_0+\nu\theta)$ being applied as a small correction determined from data which will be discussed later. The results obtained from run T_1 are

t (minutes at 2400°K)	DG/N_0 (at 2100°K)	$D(G-G_T)/N_0$ (at 2100°K)
4.7	7.67×10^{-4} sec.$^{-1}$	3.86×10^{-4} sec.$^{-1}$
23.1	4.65	0.84
45.6	3.95	0.13

All three of the observations recorded in this table, when compared with the curves of Fig. 6, are found to lie in the region where the Curves II, III and IV coincide. It was therefore assumed that the exponential type of equation such as (23) is applicable. The value of G_r was found by trial so as to make the three points corresponding to the data in the third column give a straight line when plotted on semi-logarithmic paper against the time t. The slope of this line gave $\alpha = 0.00140$ sec.$^{-1}$, from which Eq. (24) gives $D = 3.57 \times 10^{-9}$ cm^2 sec.$^{-1}$ at 2400°K.

Table III contains a summary of the absolute values of the diffusion coefficient obtained in the way just described. The logarithms of these values of D are plotted against the reciprocals of the temperatures in Fig. 7. The straight line marked D has been drawn to have the same slope as the line in Fig. 5, which corresponds to a heat of diffusion of 94000 calories per g-atom. The agreement with the observed points is very satisfactory, especially when it is considered that several different methods have been used in determining the relative and the absolute values of D.

TABLE III

Experimentally determined values of the diffusion coefficient of thorium through tungsten

Run	Temperature	Diffusion coefficient D (cm^2 sec.$^{-1}$)
N_1 to P_1	2055°K	1.1×10^{-10}
S_1	2300	1.12×10^{-9}
T_1	2400	3.57×10^{-9}
I_1 to M_1	2500	6.8×10^{-9}

The straight line in Fig. 7 gives the following equation for the diffusion coefficient at any temperature (in cm^2 sec.$^{-1}$):

$$\log_{10} D = 0.044 - 20540/T \qquad (34)$$

Table IV gives values of D calculated by this equation.

Rate of production of metallic thorium. The data furnished by low temperature activation curves enable us by Eq. (6) to calculate DG and now that we know the values of D from Table IV we can obtain the value of G. We have seen from Table II that after the filament had been heated a long time at 2500°, k_r (at 2055°) approached a limiting value of 0.000364. From the value $D = 1.12 \times 10^{-10}$ and by Eqs. (6) and (15) we thus find $G_r = 2.46 \times 10^{21}$ atoms of thorium per cm^4 at 2500°. In a similar way from data of about 20 other sets of activation runs, values of G_r for temperatures ranging from 2055° to 3000° have been

obtained. The logarithms of these values plotted against the reciprocals of the temperatures give a straight line whose equation is

$$\log_{10} G_r = 25.22 - 9620/T. \tag{35}$$

The slope of this line multiplied by 4.575 gives $Q = 44000$ calories per g-atom. Let p_r be the rate of production of thorium per unit volume throughout the filament. When the steady state has been reached in which the concentration gradient at the surface is G_r, the rate of production of thorium per unit length is $2\pi RDC_r$ and thus

$$p_r = 2DG_r/R \tag{36}$$

TABLE IV

Diffusion coefficient of thorium in tungsten and the rate of evaporation of thorium adsorbed on tungsten

T	D (cm² sec.⁻¹)	E (atoms per cm² sec.)	T	D (cm² sec.⁻¹)	E (atoms per cm² sec.)
1400°K	2.36×10^{-15}	0.445	2200°K	5.10×10^{-10}	1.61×10^{11}
1500	2.24×10^{-14}	58.5	2300	1.30×10^{-9}	1.22×10^{12}
1600	1.61×10^{-13}	4.18×10^{3}	2400	3.06×10^{-9}	7.80×10^{12}
1700	9.15×10^{-13}	1.81×10^{5}	2500	6.73×10^{-9}	4.31×10^{13}
1800	4.29×10^{-12}	5.15×10^{6}	2600	1.39×10^{-8}	2.08×10^{14}
1900	1.71×10^{-11}	1.03×10^{8}	2800	5.11×10^{-8}	3.48×10^{15}
2000	5.94×10^{-11}	1.53×10^{9}	3000	1.58×10^{-7}	3.99×10^{16}
2100	1.83×10^{-10}	1.75×10^{10}			

The temperature coefficient of p_r is thus the sum of those of D and G_r. Substituting into Eq. (36) the values of D from Eq. (34), G_r from Eq. (35) and $R = 0.00389$ cm, we obtain

$$\log_{10} p_r = 27.98 - 30160/\mathrm{T}, \tag{37}$$

p_r being expressed in atoms of thorium per sec. cm³. The heat of the reaction involved in the production of the thorium is thus $Q_r = -138000$ calories per g-atom, the negative sign indicating that the reaction involves the absorption of energy.

Although in Exps. 527 and 528 the filaments were heated for several hours per day for more than 3 months there was no indication of a falling off in the rate of production of thorium. Because of the induced evaporation, all the thorium produced at the rate p_r leaves the filament even at relatively low temperatures. The data used in calculating p_r in Eq. (37) were obtained with a filament containing 1.0 per cent of thorium oxide, corresponding to 4.4×10^{20} atoms of thorium per cm³. If the thorium were produced at a constant rate p_r the life of the thoria would be $4.4\times10^{20}/p_r$ seconds or $1.22\times10^{17}/p_r$ hours. In this way we calculate that the thoria supply should last 94000 hours at 1900°. Col. 5

of Table VIII contains data on the life at different temperatures. Considering that the rate of production of thorium must decrease as the thoria content falls off, the "life" calculated in this way probably represents the time required for the thoria to fall to one ϵth of its initial value. For different filaments, even containing the same amount of thoria, p_r varies considerably depending on the mechanical state of subdivision of the thoria in the filament and on other factors. The presence of even traces of carbon tends to reduce the thoria to thorium and greatly increases p_r. Filaments containing different amounts of thoria but otherwise alike seem in general to give values of p_r proportional to the amount of thoria.

Amounts of thorium metal present in the filaments. We see from Eq. (29) in the case of parabolic distribution, that the average concentration throughout the filament is one-half that at the center and thus according to Eq. (21) it is equal to $GR/4$. In the stationary state we may replace G by G_r which we find from Eq. (35), and thus taking $R=0.00389$ cm and by converting from atoms per cm^3 to parts by weight by dividing by 5.0×10^{22} we obtain the following average concentrations of metallic thorium in parts per million.

1800°	1900°	2000°	2100°	2200°	2400°	2800°	3000°K
1.4	2.8	5.0	8.4	14	32	118	200

Relation between induced evaporation and θ. The activation curves obtained in Exp. 528 after the filament had been well aged gave straight lines when $\theta_\infty-\theta$ was plotted on semi-logarithmic paper against the time, i.e., the data agreed with Eq. (10) which was derived on the assumption that G is constant. The foregoing analysis, however, indicates that in the neighborhood of 2100°, G should change considerably during the run if G is initially very different from the stationary value G_r.

For example in an activation run at 2100° (first part of run U_1) which followed after a flashing at 2800° for 30 seconds, θ increased from 0.01 to 0.83 in 20 minutes. The line obtained by plotting $\theta_\infty-\theta$ on semi-logarithmic paper was so nearly straight that its slope did not change more than 2 per cent in the course of its length, while calculation by Eq. (23) shows that G should have decreased about 6 per cent. Run N_1 furnishes a more striking example for the slope remained constant during the whole run of 277 minutes at 2055° although G decreased 55 per cent during this time.

This result may be explained by assuming either that θ is not strictly a linear function of log i, or that the induced evaporation is not quite proportional to θ. Taking the latter assumption as the more probable, it has been found that the data of runs U_1 and N_1, as well as several

others of a similar nature, are very satisfactorily accounted for if the factor $(1-\theta)$ in Eq. (8) is replaced by

$$f(\theta)=1-0.82\,\theta-0.18\,\theta^3, \tag{38}$$

the last 2 terms representing the induced evaporation.

Thus when θ is small, the chance is $0.82\,\theta$ that an atom of thorium in arriving at the surface shall cause the evaporation of one already on the surface. But when θ is nearly unity, the chance that an atom of thorium arriving at the surface can find a place in the surface without driving off one already present is $1.36\,(1-\theta)$. This suggests that the thorium atoms are not closely packed in the surface film even when $\theta=1$.

Normal evaporation of thorium. The actual rate of evaporation of thorium may now be calculated from the experimental data by Eq. (8). For the present, however, we do not need to assume that this rate is a linear function of θ and will therefore write the equation in the form

$$N_0\,d\theta/dt=DG\,f(\theta)-E, \tag{39}$$

where $f(\theta)$ is given by Eq. (38) but with sufficient accuracy for most purposes may be placed equal to $(1-\theta)$.

As an illustration of the method used in calculating the values of E as a function of θ, let us consider the data of run X_1 given in Table V.

TABLE V

Rate of evaporation of thorium as a function of θ

Data from Run X_1, Exp. 528 $D=1.30\times10^{-9}$ $G_T=1.09\times10^{21}$ Filament temperature 2300°K $R=0.00389$ cm

(1) t_m (min.)	(2) θ	(3) $10^4 d\theta/dt$ (per sec.)	(4) $f(\theta)$	(5) $10^{-11}DG$ (atoms cm^{-2} sec.$^{-1}$)	(6) $10^{-11}E$ (atoms cm^{-2} sec.$^{-1}$)
0	0.883	−15.95	0.152	7.86	13.25
2	0.721	−11.73	0.341	9.07	11.96
4	0.599	− 9.14	0.472	9.60	11.44
6	0.500	− 7.39	0.567	9.98	11.24
8	0.419	− 6.13	0.640	10.36	11.26
10	0.352	− 5.11	0.702	10.58	11.29
12	0.296	− 4.20	0.752	10.81	11.30
16	0.201	− 3.35	0.833	11.26	11.91
20	0.141	− 1.72	0.885	11.64	11.60
24	0.111	− 1.01	0.909	11.94	11.62
28	0.094	− 0.44	0.925	12.25	11.33

The values of θ were calculated by Eq. (1) from the saturation currents i shown in Fig. 4. The derivative $d\theta/dt$ was obtained much more accurately than would be possible from a direct plot such as Fig. 4, by plotting $(\theta-\theta_\infty)$ on semi-logarithmic paper against t so as to obtain a curve which

was very nearly straight, whose slope could thus be accurately measured at any point. According to Eq. (10) this slope is equal to k which is here considered variable and it is evident that

$$d\theta/dt = -k(\theta - \theta_\infty) \tag{40}$$

The value of the derivative found in this way is independent of the choice of θ_∞.

The values of DG in Col. 5 are calculated by means of Curve III in Fig. 6, in the following manner. In run V_1 the filament had been heated for several hours at 2250° until G had reached its stationary value G_r which by Eq. (35) is equal to 8.8×10^{20} at 2250°. In run W_1 which followed immediately after V_1, the filament was at 2105° for 196 minutes during which G fell from 8.8×10^{20} to 6.2×10^{20} while θ rose from 0.12 to 0.857. The filament was then maintained at 2000° for 47 minutes which lowered G to 6.05×10^{20} and raised θ to 0.883, and this was the condition of the filament at the beginning of run X_1 which followed. The initial value of DG at the head of Col. 5 (Table V) was obtained by multiplying G by 1.30×10^{-9}, which is the value of D at 2300° from Table IV.

From t_m, the time in minutes in Col. 1, we obtain Dt/R^2 and from Curve III in Fig. 6 find the corresponding values of RG/C_w. These are proportional to $DG-DG_r$, and thus, since we know the initial value of DG and obtain $G_r=1.09\times10^{21}$ at 2300° from Eq. (35), we calculate the remaining values of DG in Col. 5.

The rates of evaporation E given in the last column are calculated by Eq. (39) from the corresponding values of $d\theta/dt$, DG and $f(\theta)$ in columns 3, 5 and 4; N_0 being given by Eq. (15). Although θ decreases in the ratio 10 to 1, E decreases by only 15 per cent, and over most of the range may be taken as constant.

In run S_1, which is also shown in Fig. 4, a similar analysis indicates that DG at $t=5$ minutes, was 52×10^{11} and fell to 15×10^{11} at $t=106$. Notwithstanding these much higher values of DG, the values of E were not essentially different, averaging 16.3×10^{11} in the range $\theta=0.7$ to 0.2 while a similar average in run X_1 gives 11.5×10^{11}. This difference is equivalent to a change in temperature of 18° at 2300°. In run S_1 also, E was practically independent of θ.

The evaporation data from run X_1 are probably much more reliable than those from run S_1, since in the former run the term containing DG in Eq. (39) was much smaller in comparison with the $d\theta/dt$ term than in the latter run. The ratios of the values of these terms at the beginnings of these runs were 1:10 and 4.5:1 respectively. Of course the factor DG during the course of a run is subject to considerable uncertainty as it is not determined directly but is calculated

from the data of Fig. 6 and involves assumptions as to the distribution of thorium throughout the filament. The term involving $d\theta/dt$ on the other hand is found from the experimental data. Therefore it is felt that very little weight should be given to determinations of E in runs such as S_1 in which G had high values.

Two other methods were used in some experiments to determine values of E. These may be illustrated by the data of run V_1. The filament was first heated at 2800° for 30 seconds, and then run at 2195° for 60 minutes, at which time the temperature was changed to 2250°. Between the first and the 12th minute at 2195°, θ increased from 0.23 to 0.88, and the values of $(\theta-\theta_\infty)$ gave on semi-logarithmic paper a straight line whose slope corresponded to $k=35.5\times10^{-4}$ sec.$^{-1}$. The value of θ_∞ which had to be chosen to get this straight line was 0.943. Substituting these values in Eq. (14) gives $\nu_0+\nu=1.53\times10^{11}$. Assuming, in accord with the result of run X_1 that $\nu=0$ in comparison with ν_0, Eq. (13) becomes $DG=N_0k$, which gives $DG=26.8\times10^{11}$, or taking $D=4.85\times10^{-10}$ at 2195° by Eq. (34) we find $G=5.53\times10^{21}$, and $E=1.53\times10^{11}$.

During the remainder of the run at 2195°, θ increased to a maximum of 0.921 at $t=24$ minutes and then decreased slowly as in run S_1, Fig. 4. At $t=60$ min. the data showed $\theta=0.882$ and $d\theta/dt=-0.20\times10^{-4}$ sec.$^{-1}$, the filament temperature still being 2195°. When at this point the temperature was changed to 2250° the filament was rapidly deactivated, so that the curve of θ as a function of t gave a sharp kink, the slope changing abruptly from -0.20×10^{-4} to -4.5×10^{-4}. Substituting these data obtained just before (1) and just after (2) the change of temperature into Eq. (39) together with the value of N_0 from Eq. (15) we get the equations,

$$-0.15\times10^{11}=D_1Gf(\theta)-E_1$$

and

$$-3.40\times10^{11}=D_2Gf(\theta)-E_2$$

where $D_1=4.85\times10^{-10}$, and $D_2=8.22\times10^{-10}$, and $f(\theta)=0.153$ (for $\theta=0.882$). Solving these equations we find

$$G=1.35\times10^{10}E_1-0.20\times10^{21}$$

and

$$E_2=3.15\times10^{11}+1.69E_1$$

In this way by measuring the change in slope caused by a change in temperature, the value of E at one temperature can be found from that at another. If in this example we take the value $E_1=1.53\times10^{11}$ found from the first part of run V_1 we obtain $E_2=5.74\times10^{11}$ as the rate of evaporation at 2250° and $G=1.86\times10^{21}$ which is about one third the concentration gradient found at the beginning of the run.

Table VI contains a summary of the most reliable data on the rate of evaporation in Exp. 528. Col. 2 indicates the method used to determine

E, the three methods which have been described above being designated respectively I, II and III. The letter A or D is used to indicate whether the filament became activated or deactivated during the run. Col. 4 describes the condition into which the filament has been brought by its previous treatment; it gives the value of G observed in the middle of the range of θ covered by the run. In some of the runs θ varied over a wider range than indicated in Col. 5, but the value of E given in the last column is based on the observations in the range given and in this range E seemed to be substantially independent of θ.

TABLE VI

Summary of data on rate of evaporation of thorium. Experiment 528

Run	Method	Temp.	$10^{-21}G$	Range of θ	E
N_1	I−A	2055°K	1.9	0.4−0.8	6.2×10^{9}
W_1	II−A	2105	0.75	0.2−0.8	1.98×10^{10}
Q_1	I−D	2150	0.61	0.82	5.5×10^{10}
Q_1	I−D	2195	0.57	0.7−0.4	1.7×10^{11}
V_1	II−A	2195	5.5	0.2−0.9	1.53×10^{11}
V_1	III−D	2250	1.9	0.88	5.74×10^{11}
R_1	I−D	2300	0.54	0.38	1.3×10^{12}
X_1	I−D	2300	0.81	0.7−0.2	1.15×10^{12}
G_1	I−D	2400	1.7	0.6−0.4	8.8×10^{12}
U_1	I−D	2450	4.6	0.8−0.3	1.60×10^{13}

In Fig. 7 the logarithms of E are plotted against the reciprocal of the temperature. It is seen that the points lie along a straight line which corresponds to[14]

$$\log_{10} E = 31.434 - 44500/T. \tag{41}$$

Values of E calculated from this equation at intervals of 100° are given in Table IV. The slope of the line in Fig. 7 is 44500 degrees which corresponds to a heat of evaporation of 204000 calories per g-atom.

Although in the range of θ covered by the foregoing runs, E is found to be nearly constant at any given temperature it is certain from kinetic considerations that E must become proportional to θ for sufficiently small values of θ where each thorium atom must act independently of others. In fact a few runs which had been carried to particularly low values of θ gave some indication of a falling off in E. In run U_1 at 2450° E was practically constant between 0.2 and 0.8 but at $\theta=0.1$ had fallen to 65 per cent and at $\theta=0.07$ to 48 per cent of its value at $\theta=0.2$.

[14] In the abstract in the Phys. Rev. **20**, 107 (1922), the first term in the second member of this equation was given as 7.76. In the early work ν was used to express evaporation in terms of *gram atoms*$\times$cm^{-2} sec.$^{-1}$ In the abstract the definition of ν was given in atoms instead of gram atoms but by an oversight the equation was not correspondingly altered by multiplying by the Avogadro constant 6.1×10^{23}.

To get more information as to the evaporation in this region of low θ about 30 runs were carried out in Exp. 528 (after run X_1) with values of θ ranging from 0.02 to 0.3. The data were very consistent but in view of more recent experience with other types of active cathodes, it seems probable that they were subject to considerable errors due to incomplete evaporation of thorium from portions of the filament near the leads which were at a somewhat lower temperature. It is evident, because of the

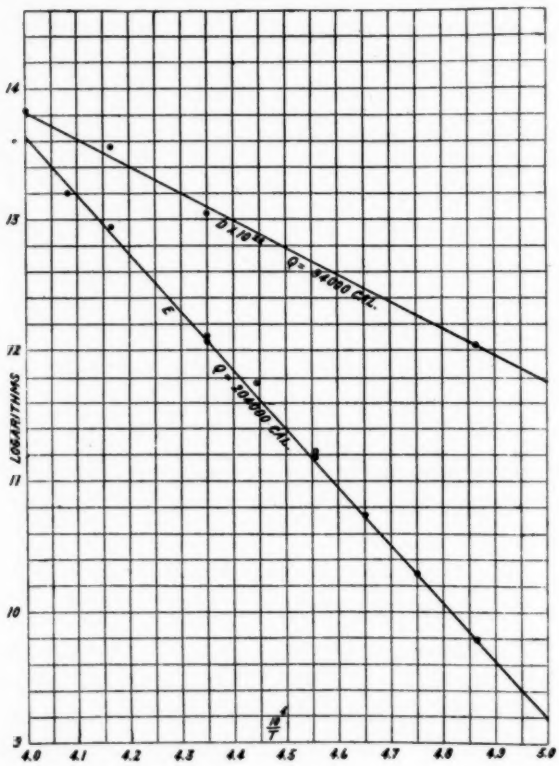

Fig. 7. Evaporation and diffusion of thorium as functions of temperature.

enormous ratio between the emission from active and deactivated filaments, that if a very short section of the filament retains its thorium, serious errors may arise in the determination of θ particularly for low values of θ. With filaments in a fairly active condition low testing temperatures such as 1450° can conveniently be used. Since the cooling effect of the leads is much more pronounced at these low temperatures than at the higher temperatures at which deactivation occurs, there is no appreciable emission from end portions of the filament which may have retained their thorium. At the higher testing temperatures used

with the low values of θ, more serious errors may occur. In future experiments all these difficulties can be avoided by dividing the anode into sections on the guard-ring principle.[15]

The general results of these runs with low values of θ are as follows. At temperatures from 2200° to 2250° E did not seem to fall off in value as θ decreased from 0.3 to 0.07 but showed a slight tendency to rise. At higher temperatures E did decrease with θ, the more rapidly the higher the temperature, but even at 2400° decreased less rapidly than in proportion to θ. As a result of these variations of E the temperature coefficient of E, and the heat of evaporation, are less than at higher values of θ.

The activation runs such as those of Tables I and II furnish some data on evaporation at high values of θ. Assuming E to be a linear function of θ, we see by Eq. (7) that the value of E for $\theta=1$ is $\nu_0+\nu$, and this may be denoted by E_1. Then Eq. (14) takes the form

$$1-\theta_\infty = E_1/N_0 k \tag{42}$$

Therefore $(1-\theta_\infty)$ plotted against $1/k$ should give a straight line passing through the origin. The observed values of θ_∞ in Table II fulfil this condition satisfactorily. The slope of the line gives E_1/N_0 from which we find $E_1=1.66\times10^{10}$. The 6th Column of Table II contains values of θ_∞ calculated by Eq. (42) with this value of E_1 and the data for k in Col. 4. The agreement with the observed values is probably within the experimental error and justifies the assumption of a linear relation between E and θ in the region from $\theta=0.94$ to 1.0. The value of E_1 from the data of Table II is 2.75 times greater than the value of E calculated from Eq. (41) for this temperature (2055°).

The data in Columns 4 and 5 of Table I were also used to calculate values of E_1 by Eq. (42). These were compared with E calculated for the same temperatures from Eq. (41) and were found on the average to be 3.12 times greater. Col. 6 Table I contains values of θ_∞ calculated by Eq. (42) from the data for k in Col. 4 by placing $E_1=3.12E$ where E was calculated by Eq. (41) for the temperature T_a (Col. 2). The agreement between the observed and calculated values of θ_∞ is excellent. This is of especial significance when it is remembered that the data of Table I were obtained with a filament containing 1.5 per cent of thoria while the filament of Table II had 1.0 per cent.

The work at low, intermediate, and high values of θ thus leads to the following conclusions. In the range from $\theta=0$ to about 0.1, E increases probably about in proportion to θ, but before 0.2 is reached increases much more slowly. Between 0.2 and 0.8, E is approximately constant,

[15] Langmuir and Kingdon, Science, **57**, 58 (1923)

showing however a tendency to increase slightly with θ at temperatures as high as 2400°, but to decrease slightly as θ increases at temperatures as low as 2200°. Above 0.8, E increases again and between 0.85 and 1.0 it increases linearly with θ until at $\theta=1$, E is about 3 times as great as in the range from 0.2 to 0.8.

Variation of heat of evaporation with θ. Dushman[16] has proposed the following empirical equation for the velocity of monomolecular reactions

$$\frac{d \log c}{dt} = \nu\epsilon^{-h\nu/kT} \tag{43}$$

where c is the concentration of the reacting substance, and $h\nu$ is the heat of reaction per molecule. Although this equation is certainly not rigorous it has been found to apply with a satisfactory degree of approximation to many fundamental processes which depend on temperature. The first member of the equation is the reciprocal of the *average life* τ of the molecules of reacting substance, and in this form the equation becomes applicable to many classes of phenomena for which we have previously had no similar relation.

The average life of a thorium atom on a surface of tungsten is given by

$$\tau = N_0\theta/E \tag{44}$$

Combining these equations and substituting $Q=Nh\nu$, where Q is the heat of evaporation of thorium from tungsten per gram atom, we obtain

$$E = (N_0 Q\theta/Nh)\epsilon^{-Q/RT} \tag{45}$$

When the values of N_0, N and h are substituted in this equation it becomes

$$E = 1.804\times10^{17} Q\theta\epsilon^{-Q/RT} \text{ (atoms sec.}^{-1}\text{ cm}^{-2}\text{)}. \tag{46}$$

We may now calculate the value of Q as a function of θ from our data on the rate of evaporation as illustrated in Table VII. The second column gives the rate of evaporation at 2300° calculated from Eq. (41) which merely summarizes the experimental data. The value at $\theta=1$ is made 3 times that in the range 0.2 to 0.8 in accordance with our

TABLE VII

Heat of evaporation of thorium as a function of θ; filament temperature 2300°K

θ	Rate of evaporation E (atoms sec.$^{-1}$ cm^{-2})	Heat of evaporation Q (calories per g-atom)
0.2	1.22×10^{12}	182,800
0.5	1.22 "	187,100
0.8	1.22 "	189,200
1.0	3.66 "	185,200

[16] S. Dushman, J. Amer. Chem. Soc., **43**, 397 (1921)

previous conclusion. The 3rd Col. gives values of Q calculated from these data by Eq. (46) but converted to calories per gram atom.

Considering the approximate nature of the Dushman equation the agreement between the calculated values of Q and the value $Q=204{,}000$ found more directly from Eq. (41) is satisfactory. It is probable that the *differences* in Q for different values of θ are accurate to much higher degree. Almost the same differences may be calculated from the same data by the Boltzmann equation. The most noteworthy feature of these variations of Q with θ is that they are so small. It indicates that the forces acting between adjacent thorium atoms on the surface is very small compared to those involved in holding these to the underlying tungsten atoms. The increase in Q between 0.2 and 0.8 corresponds to attractive forces while the decrease between 0.8 and 1.0 is evidence that the atoms are subjected to repulsive forces by the neighboring thorium atoms when they become more crowded. The effects are so small, however, that they prove that the thorium atoms are not closely packed. The results are thus in accord with the conclusion we have reached in regard to the magnitude of N_0.

Volmer and Estermann[17] have shown that mercury atoms that condense on a solid mercury crystal may retain their mobility of thermal agitation in an adsorbed film, as a kind of 2-dimensional gas. It is highly probable that thorium atoms on a tungsten surface at sufficiently high temperature are able in a similar way to move over the surface. The phenomena of induced evaporation, however, seem to indicate that this degree of mobility is very limited, for a thorium atom coming from within the filament to a surface only partly covered with thorium, would otherwise be able to push a thorium atom on the surface into an adjacent position instead of *inducing* it to evaporate. The average life of a thorium atom in a *given position* on the tungsten surface lattice (with respect to surface mobility) must therefore be long compared to the life of a thorium atom (with respect to evaporation) which has a *thorium atom* under it.

A summary of the properties of thoriated tungsten filaments is contained in Table VIII. With any such filament we may classify the phenomena into 2 groups: (I) those characteristic of the stationary state in which the metallic thorium is diffusing out of and leaving the filament at the same rate as it is produced within the filament by reduction of thoria, and (II) transient phenomena due to departures from the stationary state caused by changes in temperature or removal of thorium from the surface of the filament by sudden flashing or positive ion

[17] Volmer and Estermann, Zeitschr. f. Physik, **7**, 1 and 13, (1921)

bombardment. These transient phenomena are of two kinds: (IIa) Those in which the rate of production of thorium metal in the filament is not equal to the rate of diffusion to the surface (so called steady state), and (IIb) Those in which the rate of evaporation from the surface is not equal to the rate of arrival at the surface.

TABLE VIII

Properties of a thoriated tungsten filament in the steady state

Filament contains 1 per cent of ThO_2 Diameter 0.00389 cm

(1) T	(2) G_τ (atoms cm^{-4})	(3) θ_τ	(4) Electron emission i_τ (amp. cm^{-2})	(5) Life τ (hours)	(6) Time of recovery $1/\alpha$ (sec.)	(7) Time of activation $1/k$ (sec.)
1300°K	6.61×10^{17}	0.99997	4.14×10^{-4}		1.50×10^{10}	
1400	2.23×10^{18}	0.99975	3.12×10^{-3}		1.11×10^{9}	1.43×10^{11}
1500	6.41×10^{18}	0.99878	0.0179		1.17×10^{8}	5.23×10^{9}
1600	1.61×10^{19}	0.99528	0.0812		1.63×10^{7}	2.88×10^{8}
1700	3.64×10^{19}	0.9848	0.287		2.86×10^{6}	2.15×10^{7}
1800	7.51×10^{19}	0.9605	0.772	720,000	6.10×10^{5}	2.02×10^{6}
1900	1.43×10^{20}	0.9191	1.59	94,000	1.53×10^{5}	2.18×10^{5}
2000	2.57×10^{20}	0.8713	2.89	15,100	44,100	2.48×10^{4}
2100	4.36×10^{20}	0.781	3.43	2,897	14,300	9.48×10^{3}
2200	7.03×10^{20}	0.551	1.24	643	5,130	2.10×10^{3}
2300	1.09×10^{21}	0.139	0.114	164	2,010	531.
2400	1.63×10^{21}	0.0601	0.168	47	855	7.0
2500	2.36×10^{21}	0.0355	0.357	14.6	389	1.28
2600	3.31×10^{21}	0.0207	0.774	5.01	191	0.268
2800	6.08×10^{21}	0.0088	3.48	0.74	51	0.0161
3000	1.03×10^{22}	0.0041	13.5	0.14	17	0.0014

Col. 2 in the table gives values of G_τ (the concentration gradient at the surface when the stationary state (I) has been reached) calculated by Eq. (35). Col. 3 gives θ_τ, the fraction of the surface covered with thorium when the filament is in the stationary state (I). These data are calculated by means of Eq. (12), θ_∞ being replaced by θ_τ and G by G_τ. The values of D are taken from Table IV or Eq. (34). In accord with the experimental data discussed previously, the following convention has been adopted for values of ν_0 and ν.

Range of θ	ν_0	ν
0.0 to 0.1	0	$10\,E$
0.1 to 0.85	E	0
0.85 to 1.0	$-10.33\,E$	$+13.33\,E$

The value of E is given by Table IV or Eq. (41).

Col. 4 gives the electron emission i_τ in amperes per cm^2 at the temperature T (Col. 1) when the fraction θ_τ of the surface is covered with thorium.

Dushman[18] has shown that the electron emission from any heated metal is given by

$$i = 60.2T^2\epsilon^{-b/T} \text{ amp. cm}^{-2}, \tag{47}$$

where b is a constant which depends on the material of the cathode or the condition of its surface.

Eq. (2) may be written

$$b = b_0 + \theta(b_1 - b_0) \tag{48}$$

Dushman has obtained the values: $b_0 = 52{,}600$, $b_1 = 34{,}100$. Substituting these in Eq. (48) and then placing the value of b in Eq. (47) we obtain the data given in Col. 4.

The "stationary" emission from a thoriated filament thus reaches a maximum somewhat above 2000° and then falls gradually to that of pure tungsten.

Col. 5 gives the life of the thoria in the filament calculated from p_r (Eq. (37)) by the relation $\tau = 1.22 \times 10^{17}/p_r$. This represents the time required for the total thoria content of the filament to fall to one ϵth of its original value.

Col. 6, under the heading Time of recovery, gives the time required for transient effects of the first class (IIa) to fall to one ϵth of their value. Thus if the filament has been kept at 2000° until the stationary state has been reached, and the temperature is then changed to 2100°, G begins to change from the value 2.57×10^{20} and approaches the new stationary value 4.36×10^{20}, in such a manner that it takes 2897 seconds to go to within one ϵth of the way to the final value. The quantity α, whose reciprocal is the time of recovery, is calculated and defined by Eqs. (23) and (24). The time of recovery gives a measure of the time needed to bring the filament into the stationary state.

The last column of the table gives the time of activation, the reciprocal of the rate of activation k, defined by Eq. (10). The values in the table were calculated by means of Eq. (11), replacing G by G_r. This time of activation is the time needed for θ or i to return to within one ϵth of the way back to the "steady" value (θ_∞ or i_∞) after any small change produced by altering the temperature for such a short time that G_r is not appreciably affected. The time of activation is also a measure of the sensitiveness of the filament to effects which tend to destroy the thorium film on the surface, such as positive ion bombardment or chemical action of residual gases.

The data of Table VIII apply strictly only to a filament of the diameter given. By Eq. (36) we see that G_r should increase in proportion to R

[18] Dushman, Phys. Rev. **20**, 109 (1922), and Gen. Electric Rev. **26**, 154 (1923)

and this will change θ_r and i_r. The life τ is independent of R. By Eq. (24) it appears that the time of recovery is proportional to R^2, and by Eq. (11) the time of activation is inversely proportional to R at low temperatures and independent of R at high temperatures.

By introducing carbon into the filament, as for example by heating the filament in hydrocarbon vapors at low pressure, the value of G_r may be greatly increased, causing a corresponding increase in θ_r and i_r but a decrease in the life and in the time of activation. The decreased sensitiveness to gas effects may be of very great advantage in practical devices utilizing this type of cathode.

The writer wishes at this time to express his appreciation of the assistance and suggestions he has received from Dr. William Rogers, Mr. S. Sweetser and Dr. S. Dushman.

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May 3, 1923.

DIELECTRIC LOSSES AT RADIO FREQUENCIES IN LIQUID DIELECTRICS

By A. B. Bryan

Abstract

Dielectric losses and dielectric constants at radio frequencies for nitrobenzene, water and xylene.—The method of resistance variation was used to measure the phase difference ψ and dielectric constant K for frequencies between 2×10^5 and 14×10^5 cycles/sec. Special cells were required. (1) *Variation with frequency.* The results agree approximately with the equations: For carefully dried nitrobenzene at 30°C, $\psi=.028°+6.03\times10^4/f$; for distilled water at 23.5°, $\psi=0.8°+2.09\times10^6/f$. These indicate that in addition to the true dielectric loss there is a leakage through the liquid proportional to $1/f$. For xylene, ψ was too small to measure, less than .01° at 3×10^5 cycles. K was found to be practically independent of the frequency, being 2.24 for xylene and of the order of 100 for water. (2) *Variation with temperature, for nitrobenzene.* K decreased from 42 at 20° to 24 at 14.2°, while ψ increased in the same range in the ratio of 7 to 1. These values were obtained, however, for a sample of nitrobenzene for which ψ was 12 times as great as for a carefully dried sample.

Introduction

WHEN an alternating electromotive force is applied to a condenser a certain amount of power loss occurs due to leakage through or over the surface of the dielectric and to hysteresis, or inter-molecular friction, or some such phenomenon, in the dielectric material. This latter source of power loss is usually denoted by the term dielectric loss.

Power loss in a condenser is conveniently expressed in terms of phase difference which for small values may be obtained from the relation,

$$\psi=R\omega C$$

where R and C are the equivalent series resistance and capacity, respectively, of the condenser and ω is 2π times the frequency. For small power losses the phase difference of a condenser is the same as its power factor.

A large number of measurements of phase difference have been made on solid dielectrics of various kinds. Reference may be made to the work of Schott[1] and to the more recent investigations of the Bureau of Standards[2] and of MacLeod.[3] In the present work the measurements are extended to liquid dielectrics.

[1] Schott, Zeit. fur drahtlose Telegraphie und Telephonie. **18**, p. 82
[2] Technological Papers of the Bureau of Standards, No. 216
[3] MacLeod, Phys. Rev. **21**, 53, Jan. 1923

Experimental Method

The experimental method is one which has usually been used for previous measurements on solid dielectrics. A diagram of the circuit is shown in Fig. 1. The measuring circuit LCT is inductively coupled to L', which is part of a radio frequency oscillator. Heavy movable copper links were provided by which either the variable air condenser C_1 or the condenser to be tested C could be connected in the circuit. The high frequency current in the circuit was measured by means of the thermocouple T and the micro-ammeter G. Mercury cups MM were provided which could be connected by special high frequency resistance units of any desired value, thus making it possible to vary the resistance of the circuit. Each of these resistance units was made of a short straight piece of manganin wire, suitably mounted and of sufficiently small diameter to make negligible the change in resistance with frequency. The complete circuit was supported on ebonite posts several inches from the table to decrease losses due to leakage and to capacity to ground of

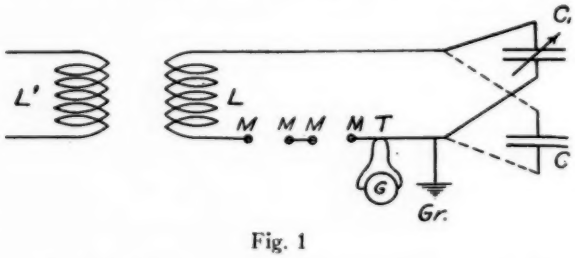

Fig. 1

various parts of the circuit, and was mounted on a rolling platform so that its distance from the oscillator could easily be changed. By thus varying the coupling between the oscillator and measuring circuit any convenient current could be obtained in the measuring circuit. The condenser C_1 is a General Radio Company "Precision Condenser" with micrometer screw adjustment and a maximum capacity of 1500 micro-micro-farads. Condensers of various forms were used for the condenser C; they will be described when the results are considered. All measurements of frequency were made with a General Radio Company "Precision Wavemeter."

In making a measurement, C is first connected in and the oscillator tuned to resonance with the measuring circuit. The total resistance of the measuring circuit, including the equivalent series resistance of C, is then determined by resistance variation. C is next replaced by C_1 which is varied until oscillator and measuring circuit are again in resonance and then the total circuit resistance is again determined as

before. The difference between this second value of the measuring circuit resistance and the value first obtained is the equivalent series resistance R of the test condenser C, the equivalent series resistance of C_1 being negligible. The capacity of C is obtained from the scale reading of the calibrated condenser C_1. The frequency having been measured with the wavemeter, the phase difference may then be calculated.

Results

Some preliminary measurements were made on several condensers having solid dielectrics. Values of phase difference and dielectric constant were obtained for frequencies between 200,000 and 1,200,000

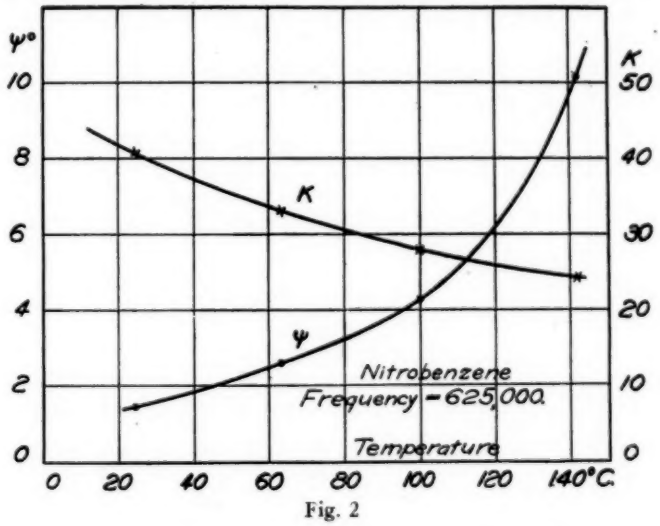

Fig. 2

cycles per second and both phase difference and dielectric constant were found to be approximately constant over that frequency range, in general agreement with the results of previous investigators.

The liquid dielectrics investigated were nitrobenzene and distilled water. Figs. 2 and 3 show the variation of ψ and the dielectric constant K with temperature and with frequency for nitrobenzene. ψ is expressed in degrees. The condenser used in these cases is shown in Fig. 4. The two plates were concentric silver cylinders A and B fixed in a glass cell. The cell had a ground glass stopper to prevent the nitrobenzene from absorbing moisture from the air. The cylinders had diameters of 3 and 4 cm and were 5 cm long. Variations of temperature were obtained by dipping the cell in an oil bath which was electrically heated. The absolute values of K for nitrobenzene are only approximate since the dimensions of the cylinders were not accurately known.

Considerable trouble was experienced in removing all the moisture from the nitrobenzene. The method first tried was to let the nitrobenzene stand some time over calcium chloride and then filter and distill it.

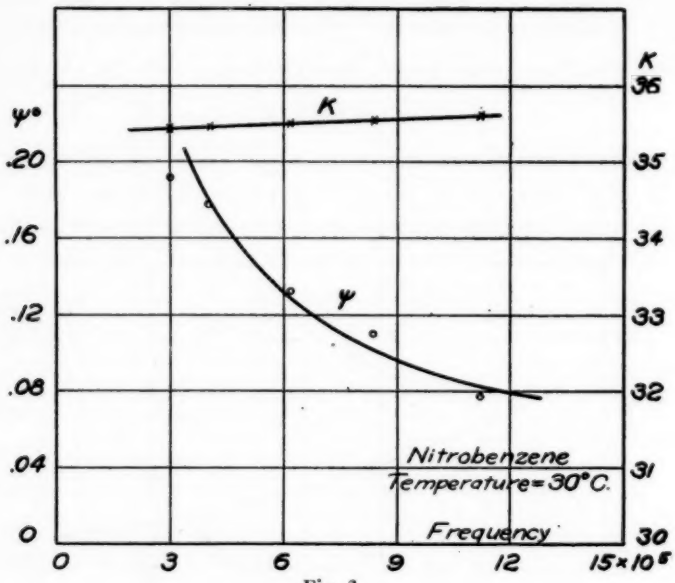

Fig. 3

The method finally used was to add red hot anhydrous copper sulphate and then distill. The nitrobenzene used to obtain the results shown in Fig. 2 had not been as thoroughly dried as that which was used for the

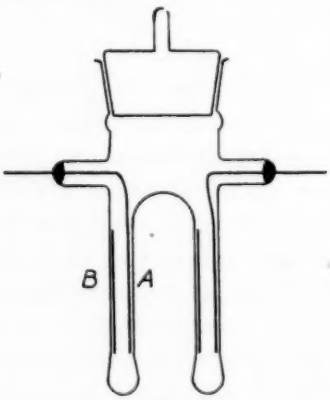

Fig. 4

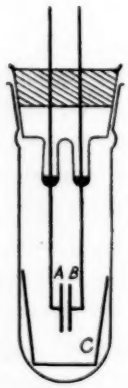

Fig. 5

results in Fig. 3, hence ψ at 30°C and 625,000 cycles is 1.6° in Fig. 2 and only 0.13° in Fig. 3. It is possible that if the nitrobenzene were perfectly dry the values of ψ would be still smaller.

The results obtained for distilled water are given in Fig. 6. The type of condenser which was finally adopted for distilled water is shown in Fig. 5. Two square platinum plates A and B, 1.6 cm square and 0.3 cm apart, formed the plates of the condenser. They were supported by platinum wires which ran down through the ground glass stopper of the glass cell. The plates dipped into the distilled water which was in a small platinum crucible C in the bottom of the cell. Several other condensers were first tried out, including the one which had been used for nitrobenzene, but it was found that the conductivity of the water was

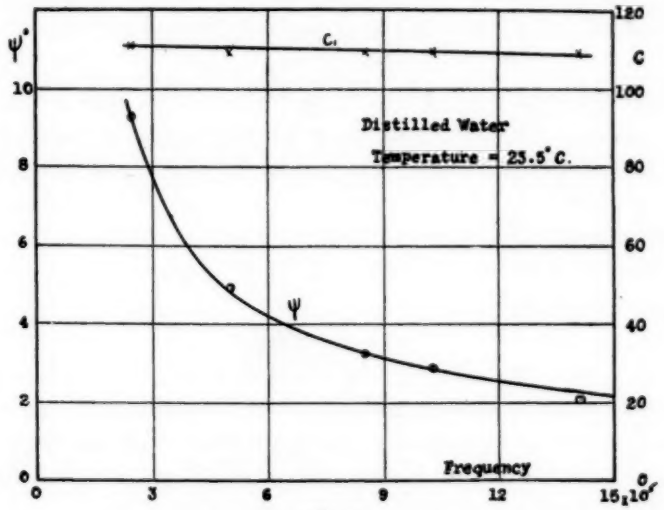

Fig. 6

too large until the above condenser was used, where the water comes in contact with platinum only. The distilled water used was obtained from an electrically heated still with a tin condensing coil.

In Fig. 6 the values of the total capacity C instead of the dielectric constant K are plotted. It is not possible to calculate K accurately because the dimensions of the plates cannot be measured accurately and because of the difficulty of allowing for the capacity of the backs of the plates and of the connecting wires. But if we assume that the given dimensions are correct and that the effect of the backs of the plates and of the connecting wires is to increase the capacity by 50 per cent, then we get $K=97$ approximately. At any rate, water has a very large dielectric constant at the frequencies used.

Several measurements were also made on *xylene* with another type of condenser but the losses in this liquid were found to be too small to be measured with the method used. For xylene the phase difference

is less than 0.01 degree at 300,000 cycles. K was independent of the frequency and equal to about 2.24.

The fact that ψ decreases rapidly with increasing frequency in the case of both liquid dielectrics, indicates that a large part of the power loss is due to leakage through the liquid. If this leakage is such as would be produced by a constant parallel resistance R_p then it may be shown that

$$\psi = 1/2\pi R_p f C$$

and the ψ due to this source will be inversely proportional to the frequency f. If we assume that ψ also has a constant component ψ_0 due to true dielectric loss, then the total phase difference will be

$$\psi = \psi_0 + A/f.$$

The curves for ψ in Figs. 3 and 6 are plotted from this equation, the constants being of course determined by selecting two points through which the curve shall pass. For water $\psi_0 = 0.8°$ and $A = 2.09 \times 10^6$. For nitrobenzene $\psi_0 = 0.0282°$ and $A = 6.03 \times 10^4$. The agreement of the experimental points with the curve is good in the case of water and only fair for nitrobenzene. In the latter case the relation between ψ and f might easily be of the form

$$\psi = A - Bf.$$

It therefore seems probable that in liquid dielectrics, as well as in solid dielectrics, the phase difference due to true dielectric loss and also the dielectric constant are practically independent of the frequency.

In conclusion, the writer wishes to express his gratitude to Professor H. A. Wilson, under whose direction this work was done.

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POLARIZATION EFFECTS SHOWN BY FILMS OF CERTAIN FUSED SALTS

By D. B. Deodhar and G. B. Deodhar

Abstract

Some experiments made by Talbot and Lord Rayleigh have been repeated and extended. A film was prepared by evaporating a solution to dryness on glass, then fusing the salt and letting it cool. In the case of potassium nitrate and potassium chlorate, when the film was placed under a microscope and between crossed nicols, Talbot and Rayleigh had observed irregularly distributed patches varying from dark to light, and variously colored. It is now found that silver nitrate and benzoic acid also show the effect. The intensity diminishes with time but the variations can still be observed after six months. A *film formed by evaporating a binary solution* of a mixture of any pair of the following: alum, boric acid, borax and citric acid, also showed the effect although films containing only one constituent were inactive. The effect is doubtless the result of mechanical strains developed on cooling the film, similar to those obtained when glass is chilled from above its softening point.

Introduction

SOME years ago the late Lord Rayleigh[1] had published a note upon a remarkable phenomenon of Newtonian colors seen by Talbot, when fused nitre was observed under crossed nicols by means of a polarizing microscope. Talbot found that the fused film appeared to be made up of crystalline plates of irregular shape, often fitted together like a tesselated pavement. If one plate was darkened by rotation of the nicol, others remained visible in varying degrees of brightness. On suitably increasing the quantity of the salt he could see the display of gorgeous colors. He also observed that the whole appearance rapidly changed in a surprising manner, and that the whole color phenomenon ceased at the end of about a quarter of an hour, the field becoming quite dark. The late Lord Rayleigh repeated this experiment with nitre and extended his observations upon potassium chlorate in practically the same way as Talbot had done, and found that the chlorate colors were less beautiful than those of the nitre. He also found that the potassium chlorate colors lasted for a longer time than nitre colors. Reinders,[2] Brauns,[3] Lehmann[4]

[1] Rayleigh, Collected papers, Vol. 6
[2] Reinders, Zeits. phys. Chem. 1912
[3] Groth, Physikalische Krystallographie
[4] Lehmann, Molekular Physik

and Tutton[5] have also touched upon these color phenomena. In the present work the observations of Talbot and Rayleigh have been repeated and extended.

Observations

(a) A few drops of *potassium nitrate* solution were laid upon a clean piece of glass, and were slowly evaporated to dryness. Then the dry substance was melted, the glass piece was removed and allowed to cool for a little while, and after some four or five minutes it was placed on the stage of a microscope having a nicol polarizer below and a nicol analyzer within the body of the instrument, set for extinction. Observations were made with sunlight and the whole field presented the appearance of a tesselated pavement of irregular boundary lines as described by Talbot. Different patches, some dark, some bright, some of varying shades of brightness and darkness, and some exhibiting brilliant Newtonian tints of varying intensity, were irregularly distributed throughout the field. On rotating the polarizing nicol through 90°, it was observed that the dark patches became bright, while the color tints changed to complementary ones. As time increased, the color effect appeared to decrease; but its rate of decrease was found to be slower and slower as time went on. After the lapse of about an hour's duration, changes in the intensity of the colors could not be detected.

(b) *Potassium chlorate* was treated in the same manner and its general behaviour was found to be the same as that of potash nitrate. The only difference detected was that the intensity of color was far stronger than that with nitre, contrary to the result obtained by Rayleigh. The rate of decrease in the color intensity with increase in time was found to be less than in the case of nitre.

(c) *Silver nitrate* was tried and found to behave as above.

(d) *Benzoic acid* showed very gorgeous colors under crossed nicols, which changed very slowly with time. It was further noted that if the heat given is just sufficient to melt the acid, the colors are very vivid; but if the heating is pushed a little too far, the color effect becomes quite dull.

(e) Another peculiarity which is observed during these experiments is, that if while observing through the eyepiece, under crossed nicols, a light scratch is made upon the fused substance on the glass piece by means of a pin point, at once colors begin to jump out of the point of disturbance in all directions, the small portion round the scratch giving an appearance of a peacock feather. The path of the pin point could be followed by the

[5] Tutton, Text book on crystallography

beautiful radiant color streaks. This effect is most striking a few minutes after melting; and when the substance becomes cold, the pin point cannot scratch and consequently the radiant color streaks cannot be observed.

(f) In order to find out the effect of time on our substances, they were carefully preserved. Unlike Talbot and Rayleigh, we found that all our preparations showed colors even at the end of six months. Of course, the intensity was not the same as that observed when the specimens were freshly prepared, but the effect was still clearly evident. This shows that the rate of diminution of intensity becomes extremely slow as time advances. These specimens are still being watched.

(g) A few drops of a solution of ordinary alum in water on clean glass were slowly evaporated to dryness, and the behaviour of the substance was observed without fusing it; but nothing could be seen under crossed nicols. Citric acid, boric acid and borax also showed the same negative behavior. However in the case of a mixture of boric acid and alum, color effects were observed, which showed the usual complementary relations on rotating the polarizing nicol. A mixture of citric acid and boric acid and of borax and citric acid also showed the same complementary color relations.

Discussion

Our observations of color effects indicate the existence of anisotropic molecular aggregates with their optic axes oriented at random; and it appears that the double refraction property may be due to the intermolecular strains and stresses developed on account of the setting of two different types of molecules in mixtures; similarly as a result of the cooling of the fused substances, unequal stresses and strains would be introduced.

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December 2, 1922.